

CANADIAN JOURNAL OF SOIL SCIENCE

VOLUME 39

February 1959 - August 1959

EDITED BY THE
AGRICULTURAL INSTITUTE OF CANADA
OTTAWA, CANADA

*Published semi-annually by the authority of the
Chairman of the National Committee on Agricultural Services*

SUBJECT INDEX TO VOLUME 39

	PAGE
Adsorption of phosphorus by four Saskatchewan soils.....	64
Alberta, A study of some profiles from major soil zones in Saskatchewan and.....	165
Alberta soils, Assessing nitrogen requirements of some.....	120
Alfalfa of phosphorus from twelve different carriers, The availability to.....	54
Alkaline permanganate oxidation of the organic matter of the A ₀ and B ₂₁ horizons of a podzol.....	44
Alluvial deposits in the Northwest Territories, Chemical, morphological characteristics of a chronosequence of soils on.....	32
Bearpaw formation, A mineralogical study of some core samples from the.....	178
Breton plot soils, Effect of cropping systems and fertilizers on mean weight-diameter of aggregates of.....	151
British Columbia soils, The occurrence of chlorite and vermiculite in the clay fraction of three.....	244
Brookston clay soil, Effects of tillage traffic on certain physical properties and crop yield on.....	98
Burning on the soil in the timber range area of Lac le Jeune, British Columbia, The influence of:	
I Physical properties.....	1
II Chemical properties.....	6
Calcite and dolomite in soils and limestones, Quantitative manometric determination of.....	197
Calibration curves of gypsum moisture blocks, Influence of bulk density and field structure of soil on the.....	12
Caribou Catena in New Brunswick, Morphology and genesis of soils of.....	222
Clay fraction of three British Columbia soils, The occurrence of chlorite and vermiculite in the.....	244
Clay-humus complexes of a chernozemic and a podzol soil, Study of the.....	136
Core samples from the Bearpaw formation, A mineralogical study of some.....	178
Cropping systems and fertilizers on mean weight-diameter of aggregates of Breton plot soils, Effect of.....	151
Dolomite in soils and limestones, Quantitative manometric determination of calcite and.....	197
Drainage following an irrigation, Rate of soil:	
I Nature of soil drainage curves.....	107
Fertilizer response by the potato, Relation of soil test values to:	
I Nitrate production and crop yield.....	144
Fox Sandy Loam, Effects of thiourea, ethyl urethane and some dithiocarbamate fungicides on nitrification in.....	235
Frost action on structure of Haldimand clay, Effect of.....	103
Fungicides on nitrification in Fox Sandy Loam, Effects of thiourea, ethyl urethane and some dithiocarbamate.....	235
Germination, Effects of fertilizers and osmotic pressure on.....	157
Haldimand clay treated with four soil additives, Note on the aggregate-size distribution and aggregate stability in.....	252
8-hydroxy quinoline (oxine) in the extraction of soil organic phosphorus, The uses of	20
In-situ technique for the quantitative determination of fertilizer phosphorus in growing plants, An.....	205

Lac le Jeune, British Columbia, The influence of burning on the soil in the timber range area of:

I Physical properties.....	1
II Chemical properties.....	6
Manometric determination of calcite and dolomite in soils and limestones, Quantitive	197
New Brunswick, Morphology and genesis of soils of Caribou Catena in.....	222
Nitrification in Fox Sandy Loam, Effects of thiourea, ethyl urethane and some dithio- carbamate fungicides on.....	235
Nitrogen requirements of some Alberta soils, Assessing.....	120
Northwest Territories, Chemical, morphological characteristics of a chronosequence of soils on alluvial deposits in the.....	32
Osmotic pressure on germination, Effects of fertilizers and.....	157
Peltier effect and its use for determining relative activity of soil water, The.....	76
Phosphorus from twelve different carriers, The availability to alfalfa of.....	54
Phosphorus in growing plants, An in-situ technique for the quantitative determi- nation of fertilizer.....	205
Podzol soil, The penetration of radioactive superphosphate into a.....	215
Potassium in soils and degree of saturation in relation to tomato yields, Exchangeable and water-soluble.....	129
Potato, Relation of soil test values to fertilizer response by the:	
I Nitrate production and crop yield.....	144
Profiles from major soil zones in Saskatchewan and Alberta, A study of some.....	165
Radioactive superphosphate into a podzol soil, The penetration of.....	215
Sand in southern Ontario, A study of the mineralogical composition of.....	185
Saskatchewan and Alberta, A study of some profiles from major soil zones in.....	165
Saskatchewan soils, Adsorption of phosphorus by four.....	64
Southern Ontario, A study of the mineralogical composition of sand in.....	185
Tillage traffic on certain physical properties and crop yield on Brookston clay soil, Effects of.....	98
Tomato yields, Exchangeable and water-soluble potassium in soils and degree of saturation in relation to.....	129
Waste sulphite liquor, Studies with:	
I Effects of waste sulphite liquor on crop yields and soil properties....	87
II Waste sulphite liquor as a soil aggregating agent.....	92
Water in soil, Horizontal movement of.....	27
Weight-diameter of aggregates of Breton plot soils, Effect of cropping systems and fertilizers on mean.....	151

AUTHOR INDEX

	PAGE		PAGE
Aylesworth, J. W.....	98	MacEachern, C. R.....	144
Beaton, J. D.....	1, 6, 54	MacKay, D. C.....	144, 215
Bentley, C. F.....	120	MacLean, A. A.....	87, 92
Bishop, R. F.....	144	McKercher, R. B.....	64
Bolton, E. F.....	98	Miller, M. H.....	205
Boswall, G. W.....	20	Nielsen, K. F.....	54
Bourget, S. J.....	12	Patry, L. M.....	165
Brydon, J. E.....	136, 197	Read, D. W. L.....	27
Chase, F. E.....	235	Rennie, D. A.....	64
Dell, Carol I.....	185	Rice, H. M.....	32, 165, 178
DeLong, W. A.....	20	Robinson, J. B.....	235
Doyle, J. J.....	87, 92	Russell, G. C.....	157
Dubetz, S.....	157	Schnitzer, M.....	44
Eaton, J. B.....	215	Skinner, S. I. M.....	197
Forman, S. A.....	165, 178	Smith, R. L.....	157
Halstead, R. L.....	129, 197	Sowden, F. J.....	136
Harward, M. E.....	244	Syngal, K. N.....	120
Heeney, H. B.....	129	Taylor, S. A.....	76
Jagues, R. P.....	235	Theisen, A. A.....	244
Korven, H. C.....	76	Toogood, J. A.....	120, 151
Leahey, A.....	32	Webber, L. R.....	103, 252
Logsdail, D. E.....	103	Webster, G. R.....	244
Lynch, D. L.....	151	Werkhoven, C. H. E.....	205
		Whiteside, E. P.....	222
		Wicklund, R. E.....	222
		Wilcox, J. C.....	107
		Wright, J. R.....	32, 44

CANADIAN JOURNAL OF SOIL SCIENCE

VOLUME 39

FEBRUARY 1959

No. 1

THE INFLUENCE OF BURNING ON THE SOIL IN THE TIMBER RANGE AREA OF LAC LE JEUNE, BRITISH COLUMBIA

I. PHYSICAL PROPERTIES¹

J. D. BEATON²

[Received for publication October 28, 1957]

ABSTRACT

Three-inch soil cores were taken in triplicate from areas that had been burned in 1943, 1945, 1945 and 1951, and from corresponding unburned areas present within each burned-over area.

Studies carried out on these cores taken from the 0 to 3-inch layer of soil revealed that, as a result of burning, there were decreases in total porosity and non-capillary porosity and an increase in capillary porosity. Field investigations showed that there was a decrease in the infiltration rate of burned soils and that there was an increase in soil temperature at a depth of 3 inches in burned soils.

INTRODUCTION

In the Douglas-fir zone of the southern interior of British Columbia, where many stands of lodgepole pine have been killed by bark beetles or by fire, large areas are covered by masses of fallen trees. Such locations are no longer easily grazed because of the inability of stock to move about readily and the difficulty in managing herds. At the same time, the routes to more desirable range areas are frequently obstructed by these barriers.

For many years stockmen have advocated the use of controlled burning to overcome such grazing problems. At the present time there are little conclusive data evaluating the effect of fire upon the soil. Consequently, this study was undertaken to determine to what extent some soil characteristics in the forest range in the vicinity of Lac le Jeune, near Kamloops, B.C., have been altered by forest fires.

Many workers have found that the temperature of the soil surface, of burned-over forest soils, to depths of 6 inches, was higher than that of the corresponding unburned soils. Frequently the increases in temperature were attributed to charcoal accumulation on the soil surface. The influence of burning on the moisture-holding capacity of forest soils has received considerable attention. The results, however, are not conclusive. It has been shown by many investigators that forest soils lose their porosity when the litter has been removed by fire. There is some evidence sug-

¹ Contribution from Field Husbandry Division, Range Experimental Farm, Kamloops, B.C. This paper includes portions of a thesis submitted by the author in partial fulfilment of requirements for the M. S. A. degree, at the University of British Columbia.

² Formerly Soil Specialist, Range Experimental Farm, Kamloops, B.C.; at present with Department of Soil Science, University of British Columbia, Vancouver, B.C.

gesting that fire has brought about the migration of colloids from the soil surface. Rideout* revealed that burning resulted in the movement of colloidal organic matter and clay particles to the subsoil. Increases in the bulk density of the soil surface of burned-over forest soils have often been reported. The infiltration capacity of burned soils is usually found to be less than that of unburned soils.

MATERIALS AND METHODS

In 1953, soil samples were collected in triplicate, using a type sampling tool fitted with 3" \times 3" metal liners. The samples represented the 0 to 3-inch depths from areas that had been burned in 1943, 1945, 1945 and 1951 and 1951 and from corresponding unburned areas present within each burned-over area. The three fires all took place within a period of 3 weeks in late July and early August, in their respective year. Approximately similar conditions of slope, exposure, drainage, topography and parent material were evident at all the sampling sites. The vegetation was nearly the same on all sites except for two burns. These exceptions were the fire of 1945 on a mixed stand of spruce, lodgepole pine, and Douglas-fir, and the 1943 burn of mature Douglas-fir. On the remaining locations lodgepole pine was the dominant type of tree cover. The soil has not been surveyed but has been tentatively classified as Grey Wooded with some evidence of Podzolized-Grey Wooded soils also being present.

By use of the 3-inch soil cores non-capillary porosity, capillary porosity and total porosity were determined after the method of Leamer and Shaw (4). The procedure outlined by Burns (1) was used for determining infiltration rates. Water infiltration measurements were made in the field with two replicates being carried out at each site. A Weston soil thermometer was used to take six replicate temperature readings at a 3-inch depth for all the sites under study.

RESULTS AND DISCUSSION

As shown in Table 1, the total porosity decreased with burning for the majority of the sites sampled. Similarly, Isaac and Hopkins (3) found that forest soils of the Douglas-fir region suffered a reduction in porosity when the litter had been removed by fire. With repeated burning, illustrated by the area burned in 1945 and again in 1951, a substantial reduction in total porosity occurred. Reductions in porosity are probably due to the destruction of the very porous organic mat resulting in exposure of the soil to the elements and the breakdown of the existing soil structure. A further reduction in porosity could result from clogging of soil pores by suspended material. On the other hand, an increase in porosity was observed in the 1943 burn of Douglas-fir. This increase in porosity may be the result of the beneficial action on soil structure of the grasses which tended to be abundant following the burn. The observed increase in porosity after burning in the stagnant lodgepole pine burn of 1951 could be explained

* Rideout, E. F. A study of slash burning and its effect on a British Columbia soil. Unpublished thesis, submitted, as partial requirement for the M.Sc. degree, to University of British Columbia. 1949.

as being the result of additions of considerable quantities of organic remains from the dead trees. Such additions would have resulted in a greater depth of porous A_0 horizon.

As a result of burning, a substantial increase in the percentage of capillary pore space was found in most of the cores studied. This increase may be partially explained by the reduction of porous litter, the destruction of soil aggregates and the subsequent washing in and plugging the larger soil pores with ash. The alkaline ash may cause dispersion of soil particles which may in turn be carried into the soil pores finally filling the larger voids. It should be pointed out that, with the removal of the A_0 horizon by fire, it is possible that a 0 to 3-inch core might include more mineral soil which has finer pores than the relatively porous organic horizon.

As a result of fire the amount of non-capillary porosity was reduced in all the samples. The removal by fire of the porous A_0 which contains many large pores should bring about a marked reduction in the percentage of non-capillary porosity. On the twice-burned site the non-capillary porosity was reduced the most.

The data presented in Table 1 reveal that burning brought about an increase in bulk density of the 0 to 3-inch layer. The greatest increase was from 0.46 for the unburned mixed stand of lodgepole pine, spruce and

TABLE 1.—THE EFFECT OF FIRE ON NON-CAPILLARY POROSITY, CAPILLARY POROSITY, TOTAL POROSITY AND BULK DENSITY OF THE SOIL¹

Description	Non-capillary porosity in per cent ²	Capillary porosity in per cent ³	Total porosity in per cent ⁴	Bulk density ⁵
1943 Burn of Douglas-fir	25.34	41.06	66.70	0.69
Unburned	33.13	31.06	64.40	0.53
1945 Burn of mixed stand	14.30	43.88	58.25	0.99
Unburned	34.69	31.51	64.85	0.46
1945 Burn of Lodgepole pine (A)	22.55	39.43	62.20	0.65
Unburned	32.85	32.45	65.25	0.49
1945 Burn of Lodgepole pine (B)	16.33	40.43	56.60	0.85
Unburned	22.08	36.40	68.25	0.64
1945 and 1951 Burn of Lodgepole pine	9.85	42.51	52.50	1.13
Unburned	22.08	36.40	68.25	0.64
1951 Burn of Lodgepole pine	25.95	40.47	67.05	0.83
Unburned	22.08	36.40	68.25	0.64
1951 Burn of stagnant Lodgepole pine	35.94	38.89	72.00	0.63
Unburned	32.81	38.00	71.00	0.39

¹ All samples taken and studied in 1953

² Coefficient of variability = \pm 10 per cent

³ Coefficient of variability = \pm 7 per cent

⁴ Coefficient of variability = \pm 4 per cent

⁵ Coefficient of variability = \pm 10 per cent

TABLE 2.—THE EFFECT OF FIRE ON THE RATE OF WATER INFILTRATION AND SOIL TEMPERATURE¹

Description	Rate of infiltration of 1000 ml. H ₂ O ²	Soil temperature at depth of 3 inches ³
	Minutes	°F.
1943 Burn of Douglas-fir Unburned	111	64
	32	58
1945 Burn of mixed stand Unburned	66	66
	21	55
1945 Burn of Lodgepole pine (A) Unburned	23	62
	16	53
1945 Burn of Lodgepole pine (B) Unburned	38	59
	15	54
1945 and 1951 Burn of Lodgepole pine Unburned	86	70
	15	54
1951 Burn of Lodgepole pine Unburned	17	63
	15	54
1951 Burn of stagnant Lodgepole pine Unburned	15	58
	15	52

¹ All determinations were performed in 1953² Coefficient of variability = \pm 13 per cent³ Coefficient of variability = \pm 2 per cent

Douglas-fir to 0.99 for the corresponding area burned in 1945. These increases in bulk density are believed to be the result of compaction of the surface soil by rain and the inclusion of more of the dense mineral soil in the 0 to 3-inch layer.

Table 2 shows that burning greatly altered the rate of infiltration on all the sites studied. The greatest reduction occurred in the 1943 fire. In the 1951 fire little or no effect was observed. It would appear that more than 2 years are necessary to affect infiltration rates. As the time required for entry of water increased with time elapsed after the fire, it is suggested that the length of exposure to the elements is one of the controlling factors in decreasing infiltration rates. The observed decreases in infiltration rates after a fire are probably due to exposure of the bare surface soil, resulting in compaction and destruction of soil structure. Although the differences in infiltration rate obtained between comparable burned and unburned areas far exceed the coefficients of variability, it should be pointed out that the validity of these results is open to some question, since the moisture tension gradients, moisture conductivities and the divergences of the moisture conductivities from uniformity were unknown.

Soil temperature at a 3-inch depth, as shown in Table 2, was found to be higher for the burned-over soils. This observation is in agreement with studies conducted in the Pacific Northwest by Isaac (2), McArdle and Isaac (5), and Isaac and Hopkins (3). The warmest soil occurred in the area that had been twice burned. Apparently with the removal of the A₀ horizon and with the falling of dead trees the soil has lost its insulating

and shading agents. As a result, the ground is subjected to more rapid changes in and/or greater extremes of temperature. The 1951 burn of lodgepole pine and stagnant lodgepole pine did not result in as large a change in temperature as did the older burns. Appreciable amounts of charcoal were observed on the soil surface in the 1951 fire; however, the shade of the remaining dead trees probably reduced the amount of solar radiation reaching the charcoal.

REFERENCES

1. Burns, Paul Y. Effect of fire on forest soils in the Pine Barren region of New Jersey. Yale Univ. School of Forestry Bull. 57. 1952.
2. Isaac, L. A. Seedling survival on burned and unburned surfaces. Forestry 28:569-571. 1930.
3. Isaac, L. A., and H. G. Hopkins. The forest soil of the Douglas-fir region and changes brought upon it by logging and slash burning. Ecology 18:264-279. 1937.
4. Leamer, R. W., and B. Shaw. A simple apparatus for measuring non-capillary porosity on an extensive scale. Agron. J. 33:1003. 1944.
5. McArdle, R. F., and L. A. Isaac. The ecological aspects of natural regeneration of Douglas-fir in the Pacific Northwest. Proc. Pacific Sci. Congr. 5:4009-4015. 1934.

THE INFLUENCE OF BURNING ON THE SOIL IN THE TIMBER RANGE AREA OF LAC LE JEUNE, BRITISH COLUMBIA

II. CHEMICAL PROPERTIES¹

J. D. BEATON²

[Received for publication November 20, 1957]

ABSTRACT

The effects of fire on certain soil chemical properties were investigated on soil samples taken from the surface organic layer (O horizon) and the immediately underlying leached mineral layer (A₂ horizon) from seven different burns and from corresponding unburned areas present within each burned-over area. Burning resulted in an increase in the pH, total phosphorus content, and CO₂-soluble calcium content of the O horizon of most of the soils studied. As a consequence of fire, the O horizon was reduced in organic matter, total nitrogen and carbonic acid-soluble phosphorous and magnesium. Most of the effects of fire upon soil chemical properties were apparently restricted to the O horizon since no significant trends were evident in the underlying A₂ horizon.

INTRODUCTION

As outlined in an earlier paper, large areas in the Douglas fir zone of the southern interior of British Columbia are no longer valuable for timber grazing because of extensive windfall coverage (2). Controlled burning has frequently been suggested as a means of overcoming such a grazing problem. Before controlled burning becomes a recognized practice in range management, the influence of burning on soil chemical properties should be established.

Studies carried out in the Pacific Northwest by Isaac and Hopkins (5) revealed that during a heavy slash fire up to 435 pounds of nitrogen per acre were lost. On Vancouver Island both Godwin (4) and Rideout (8) found that nitrification increased following a slash fire. Isaac and Hopkins (5) reported that a goodly portion or all of the unincorporated organic matter was destroyed by burning and that the incorporated organic matter was seldom reduced through burning. Tarrant (11), Isaac and Hopkins (5), Rideout (8), and Godwin (4) all found that slash burning tended to change, temporarily at least, the duff and surface soil from an acid to an alkaline condition. Rideout (8) noted that there was an initial increase in exchangeable base content of the burned surface soil. Similarly, Isaac and Hopkins (5) found an increase in the available supply of potassium and calcium in the duff and in the 0-3 inch layer. With respect to available phosphorus, Isaac and Hopkins (5) reported a decrease in the duff while Rideout (8) found that there was an initial increase in the burned surface soil.

MATERIALS AND METHODS

In 1953, soil samples were taken from the surface organic layer (O horizon) and the immediately underlying leached mineral layer (A₂ horizon) from a total of 13 pits. The relative thicknesses of these horizons are

¹ Contribution from Field Husbandry Division, Range Experimental Farm, Kamloops, B. C. This paper includes portions of a thesis submitted by the author in partial fulfillment of requirements for the M.S.A. degree, at the University of British Columbia.

² Formerly Soil Specialist, Range Experimental Farm, Kamloops, B.C.; at present with Department of Soil Science, University of British Columbia, Vancouver, B. C.

shown in Table 1. The burned O horizons are perhaps improperly designated since the organic matter content has been drastically reduced and because there are present considerable quantities of inorganic material such as ash or the inclusion of portions of the A₂ horizon due to compaction by precipitation or overgrazing. However, for the purposes of comparison, it is more convenient to use the designation O, even though it may be incorrect. The pits selected for study appeared in areas that had been burned in 1943, 1945, 1945 and 1951, 1951, and from corresponding unburned areas present within each burned-over area. Because of the difficulty in locating a suitable unburned site within the 1951 burn of lodgepole pine, the unburned area found within the lodgepole pine stand burned in 1945 and 1951 was used as a check area for both burns. The three fires, 1943, 1945, and 1951 all took place within a period of 3 weeks in late July and early August, in their respective year.

Approximately similar conditions of slope, exposure, drainage, topography and parent material were evident at all the pit sites. The vegetation was nearly the same on all sites except for two burns. These exceptions were the fire of 1945 on a mixed stand of spruce, lodgepole pine and Douglas fir, and the 1943 burn of mature Douglas fir. On the remaining locations lodgepole pine was the dominant type of tree cover. The soils have been classified as belonging to the podzolic order and have been tentatively placed in the Grey Wooded group.

The soil paste method advocated by Doughty (3) was used to prepare the soil for pH readings. The prepared soil paste was allowed to slake for 20 minutes and then pH values were determined, using a Beckman potentiometer. Organic matter determinations were carried out by the wet combustion procedure as outlined by Peech *et al.* (7). Total nitrogen was determined by the modified Kjeldhal method (1). For the measurement of total phosphorus the perchloric acid method outlined by Shelton and Harper (9) was used. The method used for extracting the plant nutrients was a modification of the CO₂-extraction procedure used by Wilcox* and the technique advocated by the National Soil and Fertilizer Research Committee (3).

RESULTS AND DISCUSSION

As shown in Table 1, all recent burns brought about positive decreases in the acidity of the O horizon. The greatest change occurred on the soil that had been twice burned, in 1945 and 1951, where pH values rose from 5.05 to 7.44. Increases in pH of the A₂ were recorded only in the older burns. The data suggested that, with an increase in time elapsed since the burn, smaller differences between burned and unburned O horizons occurred. In the case of slash burns, Tarrant (11) reported that the pH of the duff and surface soil decreased significantly with an increase in time since burning.

From Table 1, it can be seen that burning decreased the per cent organic matter of the O horizons whereas the A₂ horizons were unaffected. Since no marked changes were found below the O, it would appear that the

* Personal communication (per Stevenson, D. S.). 1953.

TABLE 1.—THE THICKNESS OF O AND A₂ HORIZONS AND THE EFFECT OF FIRE UPON THEIR pH, ORGANIC MATTER, TOTAL NITROGEN AND TOTAL PHOSPHORUS CONTENT

Description	Horizon ^{1,2}	Thick- ness (in.)	pH ³	Organic matter ⁴	Total nitrogen (N) ⁵	Total phosphorus (P) ⁶
				%	%	%
1943 Burn of Douglas Fir	O	1 $\frac{3}{4}$	5.7	16.0	0.95	0.011
	A ₂	18	5.8	0.6	0.10	0.010
Unburned	O	1 $\frac{1}{2}$	5.6	51.3	1.86	0.034
	A ₂	14	5.8	1.1	0.09	0.010
1945 Burn of mixed stand	O	$\frac{1}{2}$	5.3	11.4	0.64	0.017
	A ₂	13	5.7	0.4	0.05	0.016
Unburned	O	2	4.8	19.4	0.81	0.043
	A ₂	13	5.4	0.5	0.03	0.020
1945 Burn of Lodgepole Pine (A)	O	$\frac{3}{4}$	5.2	21.7	0.80	0.035
	A ₂	17	5.8	0.6	0.09	0.021
Unburned	O	1 $\frac{1}{2}$	4.7	73.9	1.20	0.033
	A ₂	16	5.2	0.7	0.05	0.010
1945 Burn of Lodgepole Pine (B)	O	$\frac{3}{4}$	5.7	8.9	0.52	0.109
	A ₂	16	5.9	0.5	0.07	0.013
Unburned	O	2	4.5	26.6	0.68	0.019
	A ₂	17	5.4	0.5	0.07	0.020
1945 and 1951 Burn of Lodgepole Pine	O	$\frac{1}{2}$	7.4	5.6	0.11	0.069
	A ₂	14	6.0	0.6	0.07	0.016
Unburned	O	2	5.1	29.6	1.10	0.022
	A ₂	16	6.0	0.6	0.12	0.030
1951 Burn of Lodgepole Pine	O	1	6.7	18.2	0.99	0.081
	A ₂	16	5.9	0.8	0.08	0.020
Unburned	O	2	5.1	29.6	1.10	0.022
	A ₂	16	6.0	0.6	0.12	0.030
1951 Burn of Stagnant Lodgepole Pine	O	$\frac{3}{4}$	6.2	19.6	1.79	0.054
	A ₂	18	5.7	0.8	0.07	0.016
Unburned	O	2	4.2	29.4	0.65	0.019
	A ₂	15	5.6	0.9	0.07	0.018

¹ O designation used in place of A₀. Recommendation of National Soil Survey Committee on Horizon Designation. 1957.

² Following a fire the O horizon is improperly designated; however, for ease of comparison, this designation will be used.

^{3,4,5,6} Coefficients of variability = \pm 2.5, 17.0, 25.0 and 17.0 per cent respectively.

fires lacked sufficient intensity and/or duration to destroy the incorporated organic matter. Similarly, Isaac and Hopkins (5) found that the usual heavy slash fire resulted in almost complete destruction of the duff layer with as much as 89 per cent of the organic matter originally present in the duff being destroyed.

The total nitrogen content of the O horizon decreased upon burning with the exception of the 1951 burn of stagnant lodgepole pine. Considerable variation in the content of total nitrogen was encountered in the A₂ horizon and, as a result, no apparent trend was evident. Heavy needle fall from the burned trees in the 1951 burn of stagnant lodgepole pine was believed to be responsible for the increase in the total nitrogen content of the sample of burned O horizon. Tarrant *et al.* (10) found that lodgepole pine needles contain approximately 1 per cent nitrogen, and thus a fall of these needles will contribute appreciably to the total nitrogen content as well as to the organic matter content of the burned O horizon.

TABLE 2.—THE EFFECT OF FIRE ON THE CO₂-SOLUBLE SOIL MINERALS

Description	Horizon ¹	P ²	K ³	Ca ⁴	Mg ⁵
		p.p.m.	p.p.m.	p.p.m.	p.p.m.
1943 Burn of Douglas Fir	O	10.8	24.2	26.4	21.8
	A ₂	1.5	9.5	19.5	7.2
Unburned	O	33.1	32.7	39.5	14.7
	A ₂	2.9	10.6	22.7	8.6
1945 Burn of mixed stand	O	4.8	8.8	12.3	5.1
	A ₂	0.5	5.2	9.0	4.0
Unburned	O	40.1	34.8	13.1	7.8
	A ₂	1.4	10.9	7.4	4.6
1945 Burn of Lodgepole Pine (A)	O	19.1	23.4	24.1	13.8
	A ₂	0.7	12.7	18.7	6.1
Unburned	O	32.5	49.4	24.7	23.6
	A ₂	1.7	7.0	12.8	5.9
1949 Burn of Lodgepole Pine (B)	O	2.4	5.1	13.2	5.7
	A ₂	0.6	5.4	11.2	6.9
Unburned	O	19.0	14.2	9.6	9.6
	A ₂	0.8	6.1	14.3	9.8
1945 and 1951 Burn of Lodgepole Pine	O	5.7	5.5	78.3	19.9
	A ₂	0.8	9.0	12.9	11.3
Unburned	O	20.9	28.3	17.5	12.3
	A ₂	0.7	10.3	21.0	12.5
1951 Burn of Lodgepole Pine	O	17.6	26.0	46.4	19.8
	A ₂	0.5	10.4	18.5	7.9
Unburned	O	20.9	28.3	17.5	12.3
	A ₂	0.7	10.3	21.0	12.5
1951 Burn of stagnant Lodgepole Pine	O	18.3	19.7	32.2	14.3
	A ₂	0.8	14.4	18.3	7.7
Unburned	O	17.5	20.1	18.5	4.4
	A ₂	0.7	13.0	17.8	6.9

¹ Following a fire the O horizon is improperly designated; however, for ease of comparison, this designation will be used.

^{2,3,4,5} Coefficients of variability \pm 32.0, 25.0, 18.0, and 27.0 per cent respectively.

Table 1 also shows that the total phosphorous content of both the O and A₂ horizons of the burned soils was variable. An increase in the total phosphorus content of the O horizon might be anticipated, since burning would release phosphorus from windfall material and surface litter as well as from the O horizon itself. Decreases in the total phosphorus content of the O horizon may be the result of phosphorus being lost in the smoke as described by Isaac and Hopkins (5), or it could be the effect of the wind blowing the ash and top soil as recorded by Pechanec and Stewart (6).

The effect of fire upon the CO₂-soluble minerals in the soil is recorded in Table 2. From the results presented in this table it is evident that the carbonic acid-soluble phosphorus content of the O horizon was greatly reduced as a result of burning. In addition, by comparing the total phosphorus values found in Table 1 with CO₂-soluble phosphorus values, it can be seen that the amount of phosphorus capable of being brought into solution by CO₂ extraction decreased in the case of the burned O horizons. The carbonic acid-soluble phosphorus content of the A₂ horizons was very low and consequently any changes recorded are probably of little or no significance. The observation that the availability of the phosphorus in the burned O horizons decreased is in accordance with the findings of Isaac and Hopkins (5). On the other hand, Tarrant (11) found that light slash burns increased the amount of acid-soluble P₂O₅. Decreases in the availability of phosphorus as determined by the CO₂ method could be the result of formation of relatively insoluble calcium compounds or the adsorption of phosphate ions upon charcoal which is often formed in large quantities during a fire. According to Thorne and Peterson (14), CaO-induced alkalinity will greatly reduce the availability of phosphorus. Teakle (12) demonstrated that the concentration of phosphate in the soil solution was greatly reduced as pH values rose from 4.5 to 6.5.

The carbonic acid-soluble magnesium content varied considerably in both the O and A₂ horizons. As a result of this variation no definite conclusion could be reached as to the effect of burning on the CO₂-soluble magnesium content.

REFERENCES

1. Association of Official Agricultural Chemists. Official and tentative methods of analysis of the Association of Official Agricultural Chemists. 5th ed. Washington, D. C. 1940.
2. Beaton, J. D. The influence of burning on the soil in the timber range area of Lac le Jeune, British Columbia. I. Physical properties. *Can. J. Soil Sci.* 39:1-5. 1959.
3. Doughty, J. L. The advantages of a soil paste for routine pH determinations. *Sci. Agr.* 22:135-138. 1941.
4. Godwin, Gordon. A regeneration study of representative logged-off lands on Vancouver Island. *Forestry Chron.* 14:61. 1938.
5. Issac, L. A., and H. G. Hopkins. The forest soil of the Douglas fir region and changes wrought upon it by logging and slash burning. *Ecology* 18:264-279. 1937.
6. Pechanec, J. F., and G. Stewart. Sagebrush burning—good and bad. U.S. Dept. Agr. Farmers Bull. 1948. Washington, D. C. 1944.

7. Peech, M., L. T. Alexander, L. A. Dean, and J. F. Reed. Methods of soil analysis for soil fertility investigations. U.S. Dept. Agr. Circ. 757. Washington, D. C. 1947.
8. Rideout, E. F. A study of slash burning and its effect upon a British Columbia soil. Master's thesis, Dept. Agronomy, Univ. Brit. Columbia. 1949.
9. Shelton, W. R., and H. J. Harper. A rapid method for the determination of total phosphorus in soil and plant material. Iowa State Coll. J. Sci. 15:403-413. 1941.
10. Tarrant, Robert F., Leo. A. Isaac, and Robert F. Chandler, Jr. Observations on litter fall and foliage nutrient content of some Pacific Northwest tree species. J. Forestry 49:914-915. 1951.
11. Tarrant, Robert F. Effects of slash burning on some soils of the Douglas fir region. Soil Sci. Soc. Amer. Proc. 20:408-411. 1956.
12. Teakle, L. J. H. Phosphate in the soil solution as affected by reaction and cation concentration. Soil Sci. 25:143-161. 1928.
13. The National Soil and Fertilizer Research Committee. Soil testing in the United States. 1951.
14. Thorne, D. W., and H. B. Peterson. Irrigated soils: Their fertility and management. Blakiston Co., Philadelphia, Pa. 1949.

INFLUENCE OF BULK DENSITY AND FIELD STRUCTURE OF SOIL ON THE CALIBRATION CURVES OF GYPSUM MOISTURE BLOCKS¹

S. J. BOURGET²

Canada Department of Agriculture, Ottawa, Ontario

[Received for publication June 16, 1958]

ABSTRACT

Gypsum moisture blocks were calibrated in the laboratory in undisrupted soil cores, in soil cores which had been repacked to field density, and in unpacked soil baskets. Three soil types were used. It was found that the calibration curves obtained in the repacked soil cores and in the soil baskets were different from those obtained in the undisrupted soil cores. This indicates that the disruption of both structure and bulk density influenced the calibration of gypsum blocks. The effects were greater on the fine textured than on the coarse textured soils. The influence of bulk density was not important on a sandy loam soil. The variations in soil moisture obtained ranged from 1 to 6 per cent within the available water range.

INTRODUCTION

Gypsum blocks have an important place in field work to obtain a continuous measurement of soil moisture over the growing season. Kelley *et al.* (5) compared different methods of measuring soil moisture under field conditions and concluded that gypsum blocks were the most practical instruments available for measuring moisture changes above 1 atmosphere of tension. The gypsum block method is not as accurate as the oven-drying method but is less tedious and more practical for cultivated fields. To attain the greatest degree of accuracy the blocks must be calibrated for each soil prior to installation in the field. This calibration may be made in the laboratory or in the field, in disrupted or undisrupted soil.

The procedure described by Kelley (3) for the calibration of gypsum blocks in soil baskets has been widely used. Since this procedure is not specific with respect to the degree of soil packing, the behaviour of the blocks in the baskets may be different from that in the field.

Hendrix and Colman (2) calibrated fibreglas soil-moisture units in undisrupted and in repacked soil samples. They found that soil structure, independent of bulk density, had an important influence in determining the shape of the calibration curve. The objective of the investigation reported here was to determine the effects of breaking of field structure compared to packing the soil around the blocks to field density on the shape of the calibration curves of gypsum soil-moisture blocks.

MATERIALS AND METHODS

Surface samples of Allendale sandy loam, North Gower clay loam, and Rideau clay soils were collected from fields which had been in sod for more than 5 years. Core samples were obtained, using steel cylinders 3 inches in diameter and 3 inches high. Additional samples taken with a spade were air-dried and passed through a 2-mm. sieve. All soil samples were taken in the surface 4-inch layer within an area 3 feet square.

¹ Contribution from the Division of Field Husbandry, Soils and Agricultural Engineering, Experimental Farms Service, Canada Department of Agriculture.

² Central Experimental Farm, Ottawa, Ont.

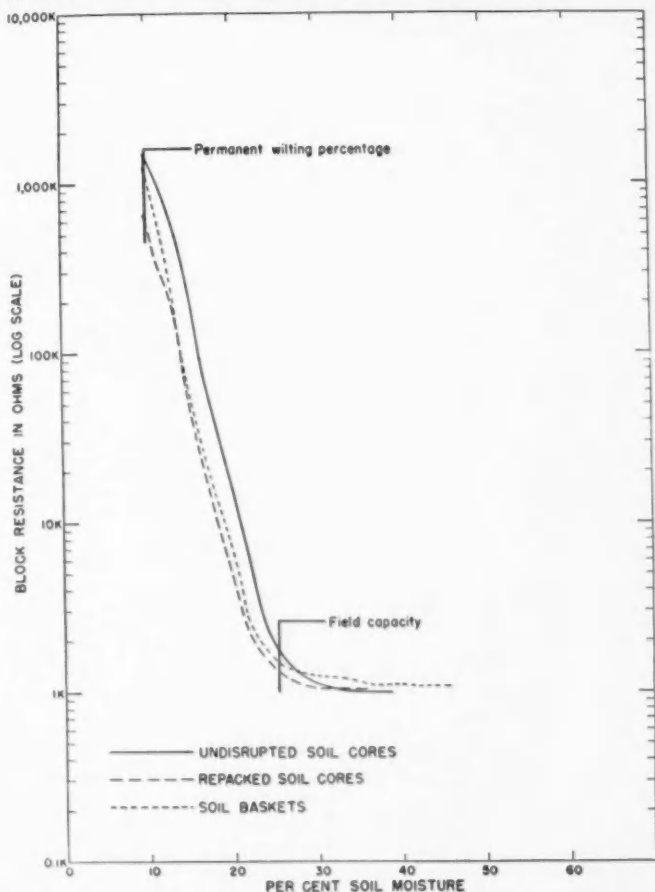


FIGURE 1. Calibration curves for gypsum moisture blocks in Allendale sandy loam soil by three methods in first run. (Each curve represents the average results for 3 blocks).

Gypsum blocks ($2.500 \times 1.375 \times 0.500$ inches in dimension) were calibrated in (1) undisrupted soil cores, 2) soil cores which had been repacked to field density, and 3) soil baskets.

The undisrupted soil samples were brought into the laboratory and enough distilled water was added to adjust the moisture content to field capacity (Buchner funnel). A rectangular-shaped metal device, with sharp cutting edges and possessing outside dimensions the same as those of a gypsum block, was pressed vertically into the central area of each soil core. In this manner a hole of suitable dimensions was made, after which a gypsum block was inserted and enough soil was packed on the top end of the block to cover it. The repacked samples were prepared by placing a gypsum block vertically in the middle of a steel cylinder and packing

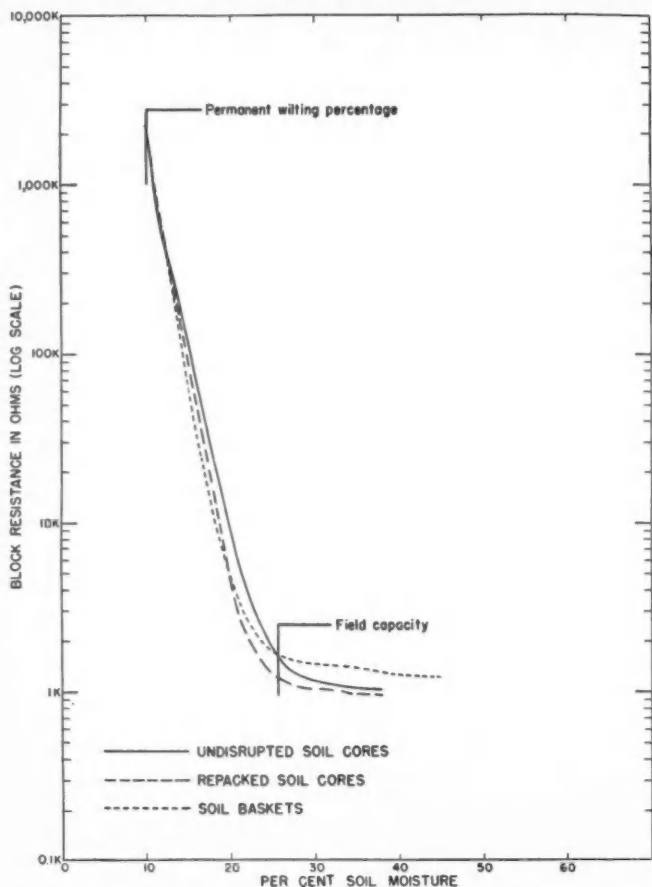


FIGURE 2. Calibration curves for gypsum moisture blocks in Allendale sandy loam soil by three methods in second and third runs. (Each curve represents the average results for 6 blocks).

enough air-dry sieved soil around it to fill the cylinder with soil at the same density as in the field. A piece of unbleached muslin was held at the bottom of the cylinder with an elastic band to keep the soil in place. The technique followed in placing the gypsum blocks in the baskets and the subsequent procedure for completing the calibration measurements, regardless of the manner of enclosing the blocks in the soil, was that described by Kelley (3).

The calibration for each method was carried out in triplicate and was repeated three times, interchanging the blocks each time on the Allendale sandy loam soil. The calibration of each block by each method was desirable since considerable variability may occur between blocks. However, after the calibrations in the Allendale sandy loam soil were run, a

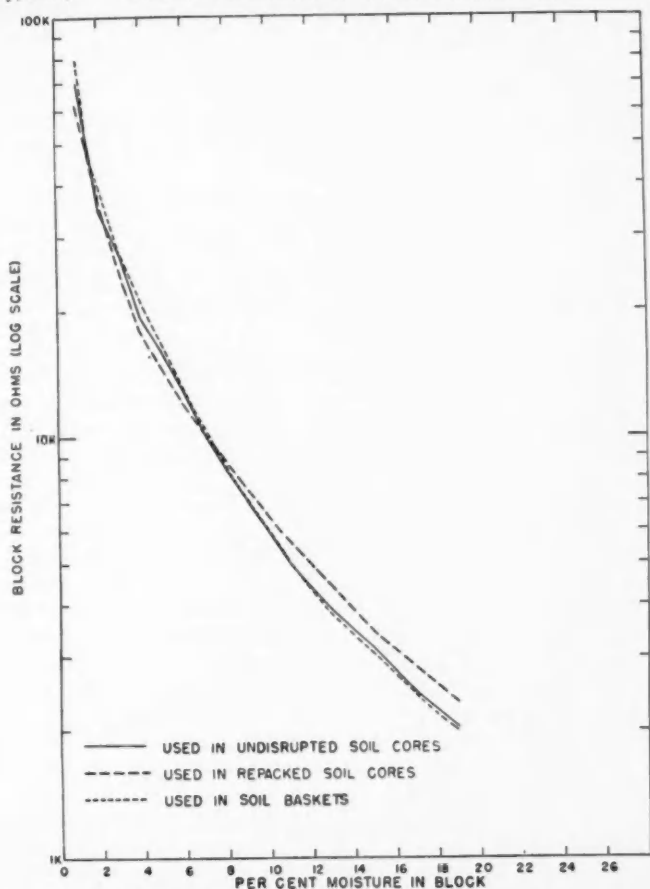


FIGURE 3. Relationship between the electrical resistance and moisture percentage of the gypsum blocks. (Each curve represents the average results for 3 blocks).

test on the variability between blocks was made by determining the electrical resistance vs. percentage of moisture for each block. The blocks were immersed in a pan of water and allowed to dry in air afterwards. Their weight and electrical resistance was determined occasionally as they dried. The calibrations for each method on the North Gower clay loam and Rideau clay soils were only carried out in triplicate without repeating the procedure. All blocks were air-dried prior to each calibration.

The bulk density was determined by dividing the oven-dry weight of a soil clod (105°C.) by its volume which was measured by immersing the clod, covered with a thin coat of wax, in water.

The total porosity was determined by saturating the soil cores under vacuum measuring the amount of water at saturation. The capillary and non-capillary porosities were determined by placing the vacuum saturated

cores on a tension table as described by Leamer and Shaw (5). A tension of 50 cm. of water was applied until the samples reached constant weight, after which they were weighed and oven-dried. The volume of water retained against 50 cm. of water tension was taken to represent the capillary pore space. The difference between the capillary and total pore space represents the non-capillary pore space.

The void ratio is equal to the quotient obtained by dividing the volume of pore space by the volume of solids. Field capacity was determined by the Buchner funnel method described by Bouyoucos (1). The permanent wilting percentage was determined by the sunflower method according to the procedure described by Richards (6).

RESULTS AND DISCUSSION

The pore space, bulk density and void ratio of undisrupted and repacked soil cores, and of soil in baskets used for gypsum block calibrations are reported in Table 1. The total porosity and void ratio values for the undisrupted soil cores were similar to the corresponding values obtained for the repacked soil cores. This was expected, since the samples had the same bulk density. The non-capillary porosity of the undisrupted soil cores was greater than that of the repacked soil cores, indicating a better structural condition in the undisrupted soil. The soils in the baskets had the lowest values for bulk density and the highest values for void ratio. They also gave the highest values for total and non-capillary porosity.

The structural breakdown resulting from packing the disrupted soils to the same density as the undisrupted samples indicated by the decrease in non-capillary porosity was more pronounced on the Allendale sandy loam than on the clay soils. These data indicate that marked differences in structure existed between the soil samples prepared by the different methods.

The results for the calibration of gypsum moisture blocks in undisrupted soil cores, in repacked soil cores and in soil baskets, obtained by the first run on the Allendale sandy loam soil are shown in Figure 1. The calibration curve for the repacked soil cores was similar to that for the soil

TABLE 1.—POROSITY, BULK DENSITY AND VOID RATIO OF THE ALLENDALE SANDY LOAM, NORTH GOWER CLAY LOAM, AND RIDEAU CLAY SOILS PREPARED FOR GYPSUM BLOCK CALIBRATION BY THREE DIFFERENT METHODS

(Mean values for three samples)

Soil	Method	Total porosity	Non-capillary porosity	Capillary porosity	Bulk density	Void ratio
Allendale sandy loam	Undisrupted soil cores	58.3	15.3	43.0	1.35	1.40
	Repacked soil cores	58.2	1.9	56.3	1.36	1.39
	Soil baskets	68.6	25.4	43.2	1.15	2.19
North Gower clay loam	Undisrupted soil cores	61.8	16.4	45.4	1.35	1.62
	Repacked soil cores	62.3	9.6	52.7	1.33	1.68
	Soil baskets	85.4	49.2	36.2	0.96	5.87
Rideau clay	Undisrupted soil cores	61.4	22.9	38.5	1.35	1.74
	Repacked soil cores	61.6	16.2	45.4	1.39	1.61
	Soil baskets	90.7	55.8	34.9	0.98	15.70

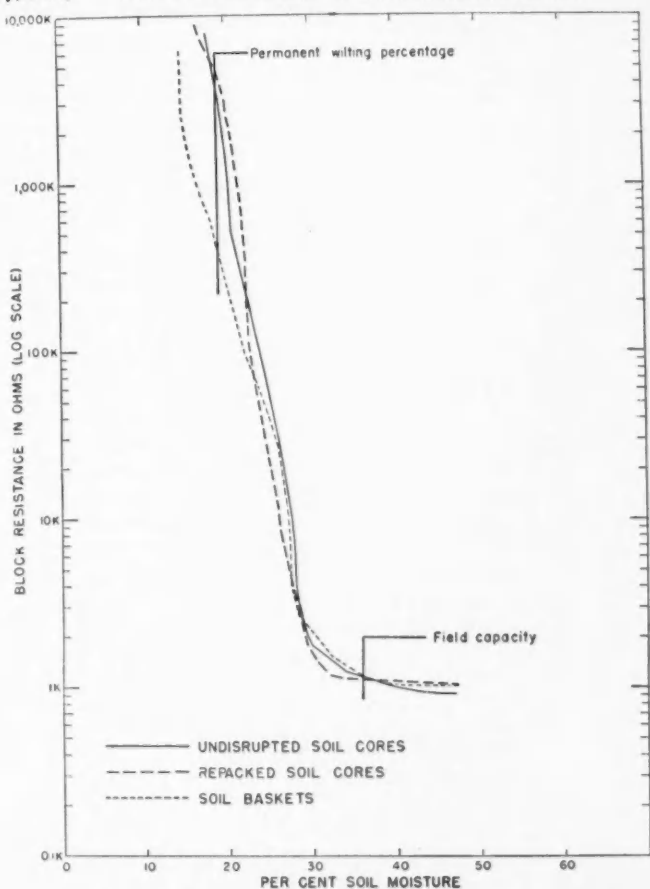


FIGURE 4. Calibration curves for gypsum moisture blocks in North Gower clay loam soil by three methods. (Each curve represents the average results for 3 blocks).

baskets. This similarity suggests that either the degree of soil packing around the blocks had little effect on the calibration or the density of the soil adjacent to the block was below the average density of the repacked core as a whole. Within the available soil moisture range, the curves for the repacked soil cores and the soil baskets showed lower moisture percentage values than the curve for the undisrupted soil cores. The differences in moisture content resulting from disrupting the soil was approximately 2 per cent. This indicates that soil structure was the most critical factor in determining the shape of the calibration curve.

The calibration curves based on the results for the second and third runs on the Allendale sandy loam soil are shown in Figure 2. These results were combined because of the close agreement between curves for the same method. These curves, based on repetition of the experiment with inter-

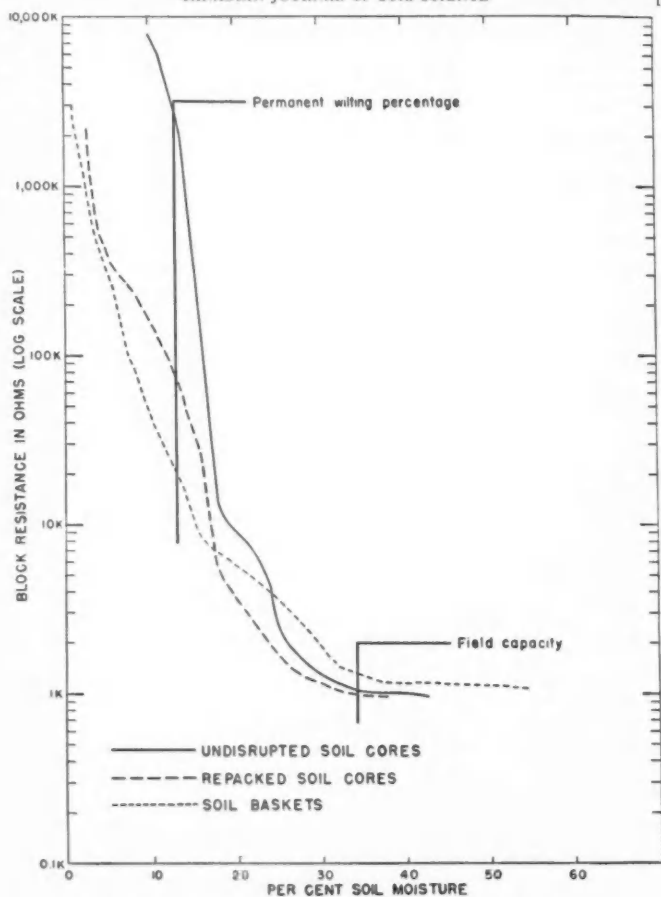


FIGURE 5. Calibration curves for gypsum moisture blocks in Rideau clay soil by three methods. (Each curve represents the average results for 3 blocks).

changing of the gypsum blocks, show that the effect of disruption of soil structure on the moisture percentage values was only apparent in the higher range of available soil moisture. It is possible that the effect of disruption of soil structure shown in Figure 1 was the result of variability in gypsum blocks. This is unlikely, however, since the curves for the repacked soil cores and the soil baskets were similar.

Figure 3 shows the relationship between the electrical resistance and the moisture percentages for the nine gypsum blocks used. The relationship is given as an average of three replicated blocks as they were used for the remainder of the experiment. The blocks used in the undisrupted soil cores and in the soil baskets were very closely related. The blocks used in the repacked soil cores showed a maximum variation of 1 per cent in moisture percentage near saturation. In general, the variability was small,

indicating that the blocks were quite uniform. The calibrations in the other two soil types were run in triplicate but were not repeated because of the slight variability between blocks.

The calibration curves of gypsum moisture blocks in undisrupted soil cores, in repacked soil cores and in soil baskets for the North Gower clay loam soil, are shown in Figure 4. All three calibration curves show close agreement at high moisture percentages in the available water range. A variation in soil moisture content of 0 to 3 per cent as indicated by these three methods occurred at lower moisture percentages in the available range.

The results obtained by the three calibration methods on the Rideau clay soil are shown in Figure 5. The three curves vary considerably and this variability increases as the soil moisture percentages decrease. This seems to indicate that soil shrinkage contributed to erratic readings, since the surface of contact between the soil and the block might have decreased. Both the curves obtained in the disturbed unpacked and in the disturbed repacked soils deviate widely from the one in the undisrupted soil. The soil moisture percentages obtained by the three curves varied from 3 to 6 per cent within the available water range.

The results obtained in this experiment indicate that disruption of soil structure and bulk density influenced the moisture percentage values considerably. This influence was greater on the fine-textured than on the coarse-textured soils. The differences obtained are especially important if one considers that they often occurred in the lower end of the available water range. To avoid this effect of structure and bulk density it follows that care should be taken to install the blocks in undisrupted soil. This can be accomplished by inserting the blocks in holes of the same size as the blocks made on the side of a pit or auger hole dug vertically in the soil, and repacking with the disturbed soil at the same field density.

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to A. J. MacLean, Chemistry Division, Science Service, for his constructive criticism; to K. B. Dow for the laboratory care of the experiment, and to the Soil Cartographic personnel for assistance in the preparation of the graphs.

REFERENCES

1. Bouyoucos, C. J. A comparison between the suction method and the centrifuge method for determining the moisture equivalent of soils. *Soil Sci.* 40:165-172. 1935.
2. Hendrix, T. M., and E. A. Colman. Calibration of fiberglass soil moisture units. *Soil Sci.* 71:419-427. 1951.
3. Kelley, O. J. A rapid method for calibrating various instruments for measuring soil moisture in situ. *Soil Sci.* 58:433-440. 1944.
4. Kelley, O. J., A. S. Hunter, H. R. Haise, and C. H. Hobbs. A comparison of methods of measuring soil moisture under field conditions. *J. Amer. Soc. Agron.* 38:759-784. 1946.
5. Leamer, R. W., and B. Shaw. A simple apparatus for measuring non-capillary porosity on an extensive scale. *J. Amer. Soc. Agron.* 33:1003-1008. 1941.
6. Richards, L. A. (ed.). *Diagnosis and improvement of saline and alkali soils.* U.S. Regional Salinity Lab., Riverside, Calif. 1947.

THE USE OF 8-HYDROXY QUINOLINE (OXINE) IN THE EXTRACTION OF SOIL ORGANIC PHOSPHORUS¹

G. W. BOSWALL² AND W. A. DELONG³

Macdonald College, Quebec

[Received for publication June 13, 1958]

ABSTRACT

A mild laboratory procedure, employing oxine in a water-benzene system, for the release of organic phosphorus from two unimproved pasture soils differing widely in total phosphorus, ratio of organic to inorganic phosphorus, pH, calcium content and clay content, is described.

Data are presented showing the influence of the following factors on the amount of phosphorus released: soil to water ratio, the pH of the extraction medium, and the soil pretreatments. Under the more favourable conditions the two soils released 75 and 86 per cent of their total organic phosphorus respectively.

INTRODUCTION

The surface layers of many mineral soils contain from 30 to 50 per cent of the total phosphorus in the organic form (4, 6), and the desirability of considering this fraction in predicting the plant-available phosphorus has been emphasized (7). The observation that the amount of organic phosphorus is lower in cultivated soils than in adjacent virgin areas suggests that it contributes to the nutrition of crop plants (15), and therefore merits more consideration than it has received in the past.

Most procedures for the extraction of organic phosphorus involve a treatment with one or more reagents designed to remove all the organic phosphorus without changing any of it to the inorganic form. Usually the soil receives an acid pretreatment to remove cations, followed by an alkaline extraction with ammonium or sodium hydroxide to remove the greater part of the organic phosphorus. Such procedures are rather harsh and may cause hydrolysis and/or other chemical changes. Such changes are undesirable whether the extracts are being used to estimate the soil organic phosphorus content or to study the nature and identity of the compounds extracted, so that the need for a milder extraction procedure is indicated.

The observations of Dion and Mann (5) that pyrophosphate was much more efficient in the extraction of manganese from soil than orthophosphate led Bremner and Lees (2), who were interested in mild extractants for soil organic matter, to test the extractive capacities of neutral solutions of sodium salts of organic and inorganic acids. Sodium pyrophosphate, sodium oxalate, sodium fluoride and sodium citrate were found to be the most effective of the reagents tested, although less organic matter was extracted than by any other alkali. These results, together with those of Heintze and Mann (9), which showed that solutions of hydroxy acids were almost as effective as pyrophosphates, indicated that the organic

¹ Contribution from the Faculty of Agriculture, McGill University, Macdonald College, Que., Canada. *Journal Series No. 422.* Financial support by the Quebec Department of Agriculture, and the Canada Experimental Farms Service is gratefully acknowledged.

² Formerly post-graduate research assistant, Macdonald College.

³ Professor of Agricultural Chemistry, Macdonald College.

matter is intimately associated with metallic cations and that its solubility in neutral reagents is largely determined by the nature of this association. Further, the efficiency of a neutral salt extractant appeared to depend on the ability of its anions to remove interfering metals either as insoluble precipitates or as soluble co-ordination complexes (1). Martin and Reeve (12) reported the use of aqueous or aqueous-acetone solutions of the chelating agents cupferron, oxine, and acetyl-acetone for the extraction of organic matter from the B horizon of podzolic soils.

Oxine has been used by some workers in soil phosphorus studies to block fixation of the phosphorus during extraction (8, 13, 16). Saunders and Williams (13) found that oxine interfered in the analytical determination of organic phosphorus.

The objective of this investigation was to utilize oxine in the release of the organic phosphorus compounds occurring in soils.

MATERIALS AND METHODS

The soil samples used in this investigation were obtained from the top 6 inches of long established unimproved pastures on the Greensboro loam (3) and the St. Bernard clay loam (10). Some characteristics of these soils are presented in Table 1.

The colorimetric method used to estimate phosphorus was that described by Martin and Doty (11). The total soil phosphorus was determined after treatment by the Sherman method (15). Total soil organic phosphorus was estimated by the ignition and difference method of Saunders and Williams (13).

In order to determine the inorganic phosphorus in highly coloured soil extracts it was necessary to acidify to pH 1.5 to precipitate much of the organic matter. Following centrifugation aliquots of the supernatant liquid were taken for the estimation of inorganic phosphorus. Total phosphorus was determined in extracts following digestion of aliquots with perchloric acid until white fumes were evolved. Originally nitric-sulphuric acid digestions were used; but it was found that the sulphuric acid interfered with the extraction of the phosphomolybdate into the isobutanol-benzene phase in the Martin and Doty procedure. This interference resulted in low values for the phosphorus. All pH measurements were made with a Beckman model G pH meter.

TABLE 1.—SOIL CHARACTERISTICS

Texture	Greensboro loam	St. Bernard clay loam
pH	4.5	7.0
Total Ca O — %	0.5	3.0
Total phosphorus (P) — p.p.m.	564	1363
Organic phosphorus (P) — p.p.m.	353	522
Organic phosphorus (P), as per cent of total	62%	38%

The general procedure employed in the extraction of organic phosphorus using oxine was as follows: Soils were converted to the ammonium form for all extractions except in those experiments where acid pretreatments were used. To a suitably sized flask the soil and water were added and the pH of the suspension adjusted to the desired value with either dilute ammonium hydroxide or acetic acid. A 2.5 per cent solution of oxine in benzene then was added and the flask placed on a mechanical rotary shaker. The pH was checked periodically and maintained within ± 0.2 of the required value. At the completion of the shaking the liquid phases were separated in separatory funnels and the benzene layer washed several times with water to remove the soil and the entrapped aqueous extract. The aqueous phase and combined washings were then centrifuged until clear.

RESULTS AND DISCUSSION

The efficiency of the procedure for extraction of soil phosphorus was tested in a long-term experiment. For this purpose 5-gram samples of each of the two soils which had been converted to the ammonium form were placed in flasks with 50 ml. water and 20 ml. of 2.5 per cent oxine-benzene solution and shaken for 805 hours, the pH of the aqueous phase being maintained at approximately 6.5. The aqueous phase was sampled periodically during the run and distilled water was added to the flask to maintain the soil/water ratio. These prolonged extractions released 63 per cent and 15.4 per cent respectively of the total phosphorus in the Greensboro and St. Bernard soils. The concentration of total phosphorus in the aqueous phases always reached approximately 7 and 4 p.p.m. respectively. These data suggested an equilibrium state for each soil/water system; therefore the effect on extraction of widening the soil/water ratio was investigated. The results of these experiments are presented in Table 2.

TABLE 2.—PHOSPHORUS RELEASED AT pH 6.5 AT VARIOUS SOIL/WATER RATIOS DURING A 24-HOUR EXTRACTION, AS PER CENT OF THE TOTAL INORGANIC AND TOTAL ORGANIC PHOSPHORUS IN THE SOIL

Soil/water ratio	Greensboro		St. Bernard	
	Inorganic %	Organic %	Inorganic %	Organic %
1:15	7.1	27	6.2	6.9
1:50	13.7	25	15.5	8.4
1:100	16.6	26	21.2	9.2

TABLE 3.—PERCENTAGE OF SOIL ORGANIC PHOSPHORUS RELEASED WHEN EXTRACTED AT pH 6.5 AND 9.3 WITH AND WITHOUT BENZENE-OXINE FOR 5 HOURS

pH	Greensboro		St. Bernard	
	Water %	Benzene-oxine %	Water %	Benzene-oxine %
6.5	1.3	6.8	3.6	5.0
9.2	7.6	47.0	6.3	14.8

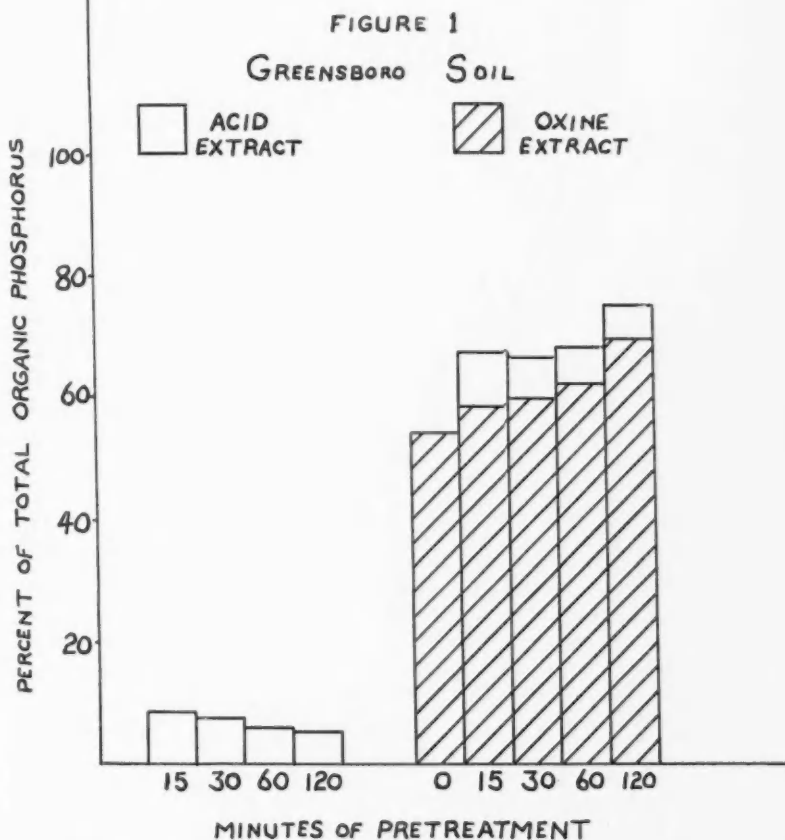


FIGURE 1. Effect of pretreatment with acid on release of organic phosphorus from Greensboro soil.

These results indicated that the amount of organic phosphorus released was not influenced to any large extent by varying the soil/water ratio, although the St. Bernard soil showed a small increase from 6.9 to 9.2 per cent as the ratio changed from 1:15 to 1:100. However, the release of inorganic phosphorus from both the Greenboro and St. Bernard soils was more than doubled and tripled respectively as the soil/water ratio was changed from 1:15 to 1:100.

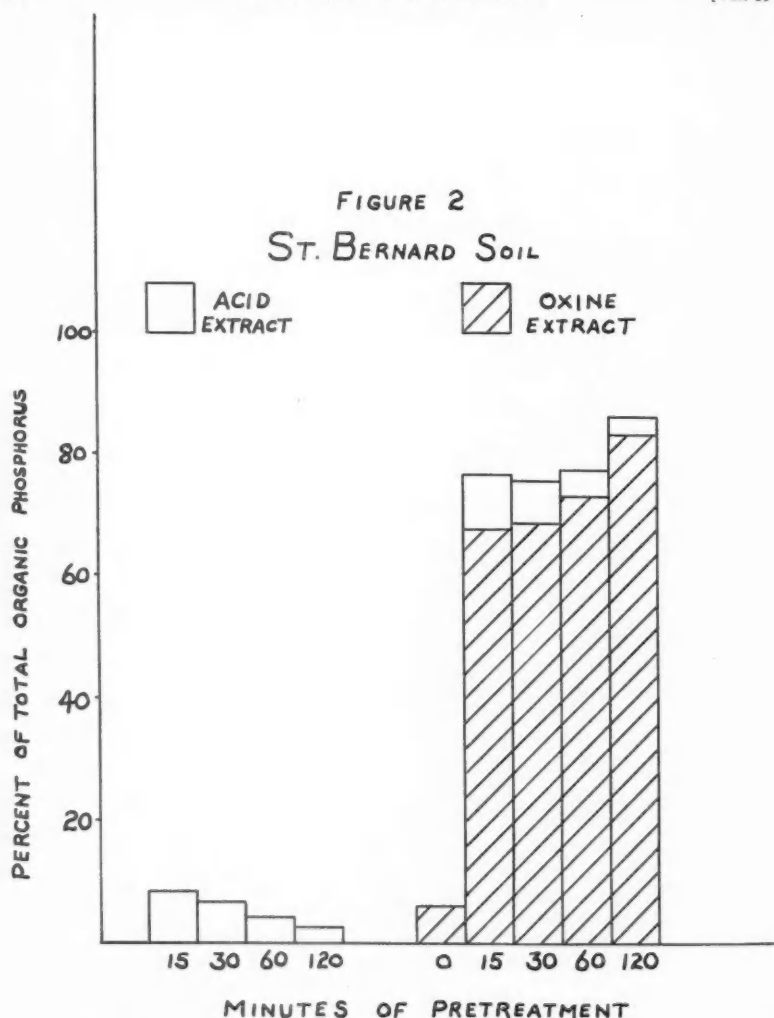


FIGURE 2. Effect of pretreatment with acid on release of organic phosphorus from St. Bernard soil.

The influence of pH level in the aqueous phase and of the presence of oxine on the release of organic phosphorus also was investigated. The results are given in Table 3.

With water only both soils released more organic phosphorus at the higher pH level. The Greensboro soil gave about a sixfold increase at pH 9.2, the St. Bernard soil only a twofold increase. Similarly, the use of benzene-oxine was responsible for an increased organic phosphorus release from both soils, the increase for the Greensboro soil was about

sevenfold, while that for the St. Bernard soil was only about threefold. It is apparent that there was a marked positive interaction between pH and the use of benzene-oxine in release of phosphorus from the Greensboro soil. The release of organic phosphorus from this soil was about 36 times greater at pH 9.2 with benzene-oxine than it was at pH 6.5 with a water extraction. The St. Bernard soil showed a similar trend but the increased release of organic phosphorus at the higher pH with benzene-oxine was not nearly as pronounced as for the Greensboro soil.

In an attempt to increase the release of organic phosphorus, particularly from the St. Bernard soil, the soils were pretreated with 0.5 N HCl for various lengths of time on a rotary shaker, washed with distilled water to remove chloride, and then extracted with benzene-oxine at pH 9.2 for 18 hours. The percentages of total organic phosphorus released by acid pretreatment for varying lengths of time, and by a subsequent 18-hour oxine extraction, are shown in Figures 1 and 2.

Figure 1 shows that the amount of organic phosphorus extracted from the Greensboro soil by the acid pretreatment decreased with the time of contact, and that the subsequent release of organic phosphorus in the oxine extraction increased with increased time of acid pretreatment. The increase of organic phosphorus released following a 2-hour acid pretreatment amounted to about 15 per cent of the total organic phosphorus in the soil.

Figure 2 shows that the response of the St. Bernard soil to the acid pretreatment is very similar to that of the Greensboro soil in that the organic phosphorus removed decreased with the time of acid pretreatment. However, in the case of the St. Bernard soil, the release of organic phosphorus to the oxine extraction following the acid pretreatment is very pronounced. Thus, the 15-minute acid-pretreated soil released more than ten times as much organic phosphorus as soil which had received no acid pretreatment. The increase of organic phosphorus released following a 2-hour acid pretreatment amounts to about 76 per cent of the total soil organic phosphorus. The total amount of phosphorus released by both the acid and oxine extractions amounted to 75 per cent and 86 per cent of the total organic phosphorus in the Greensboro and St. Bernard soils, respectively.

Investigation of the distribution of phosphorus between the aqueous and the benzene phases after this extraction technique had been applied to the Greensboro soil showed that a small amount of phosphorus was present in the benzene phase. However, on the assumption that all of the phosphorus in that phase was in organic form, calculations showed that at least 90 per cent of the organic phosphorus released remained in the aqueous phase.

The proportions of the total organic phosphorus released into the aqueous phase by benzene-oxine extraction at pH 9.2 following a mild acid pretreatment approaches that obtained by older more drastic extraction procedures. The aqueous solution obtained by the extraction method here described has the advantage of a very low content of cations. Further, no extraneous anions have been introduced which might interfere with subsequent attempts to identify the phosphorus compounds extracted.

REFERENCES

1. Bremner, J. M. A review of recent work on soil organic matter. II. *J. Soil Sci.* 5: 214-232. 1954.
2. Bremner, J. M., and H. Lees. Studies on soil organic matter: II. The extraction of organic matter from soil by neutral reagents. *J. Agr. Sci.* 39:274-279. 1949.
3. Cann, D. B., and P. Lajoie. Soil survey of Stanstead, Richmond, Sherbrooke and Compton counties in the Province of Quebec. Canada Dept. Agr. Publ. 27. 1942.
4. Dickman, S. R., and E. E. DeTurk. A method for the determination of the organic phosphorus of soils. *Soil Sci.* 45:29-39. 1938.
5. Dion, H. G., and P. J. G. Mann. Three-valent manganese in soils. *J. Agr. Sci.* 36: 239-245. 1946.
6. Dyer, W. J., and C. L. Wrenshall. Organic phosphorus in soils. I. The extraction and separation of organic phosphorus compounds from soils. *Soil Sci.* 51:159-170. 1941.
7. Eid, M. T., C. A. Black, and O. Kempthorne. Importance of soil organic and inorganic phosphorus to plant growth at low and high soil temperatures. *Soil Sci.* 71:361-370. 1951.
8. Ghani, M. O. Use of 8-hydroxy quinoline as a means of blocking active iron and aluminum in the determination of available phosphoric acid of soils by dilute acid extraction. *Indian J. Agr. Sci.* 13:652-655. 1943.
9. Heintze, S. H., and P. J. G. Mann. Soluble complexes of magnanic manganese. *J. Agr. Sci.* 37:23-26. 1947.
10. Lajoie, P., and R. Baril. Soil survey of Montreal, Jesus, and Bizard Islands in the Province of Quebec. Canada Dept. Agr. Publ. 32. 1954.
11. Martin, J. B., and D. M. Doty. Determination of inorganic phosphate. Modification of isobutyl alcohol procedure. *Anal. Chem.* 21:965-967. 1949.
12. Martin, A. E., and R. Reeve. Extraction of organic matter from podzolic B horizons with organic reagents. *Chem. & Ind.* 356. 1956.
13. Saunders, W. M. H., and E. G. Williams. Observations on the determination of total organic phosphorus in soils. *J. Soil Sci.* 6:254-267. 1955.
14. Sherman, M. S. Colorimetric determination of phosphorus in soils. *Ind. Eng. Chem. Anal. Ed.* 14:182-185. 1942.
15. Thompson, L. M., and C. A. Black. The mineralization of organic phosphorus, nitrogen, and carbon in Clarion and Webster soils. *Soil Sci. Soc. Amer. Proc.* 14:147-151. 1950.
16. Williams, Colin H. Studies on soil phosphorus. I. A method for the partial fractionation of soil phosphorus. *J. Agr. Sci.* 40:233-242. 1950.

HORIZONTAL MOVEMENT OF WATER IN SOIL¹

D. W. L. READ²

Canada Department of Agriculture, Swift Current, Saskatchewan

[Received for publication December 21, 1958]

ABSTRACT

A laboratory experiment was conducted to determine the rate of extraction and the distance water will move in a horizontal radial system. An absorber was placed in the centre of a layer of soil 5 cm. deep. Extractions were made from three soils, loam, sand, and clay, which were at soil moisture tensions of zero to 450 cm. of water tension. Over this moisture range water moved to the absorber from at least 14 cm. away. No appreciable soil moisture tension gradients developed in the soil, even though there was a difference between the tension in the absorber and that in the cup.

INTRODUCTION

The flow of water in soil has been studied extensively for many years, (2, 3, 5, 9, 11, and 14). Darcy's law can be used with a fair degree of accuracy to calculate movement in saturated soil; however, when tension develops in the soil water system, as in unsaturated soil, this law is difficult to apply. In unsaturated soil the flow is no longer directly proportional to the pore size and gradient but also depends on the thickness of the water film around the soil particles. The film thickness varies inversely with the degree of unsaturation in the soil.

The availability of water to plants depends partly on the ability of water to move through the soil to the plant roots. Under normal conditions of plant growth all this movement must occur in unsaturated soil. Two factors are important in this moisture movement—the rate of movement, and the total amount that will move to the plant root. The amount of water that will move depends on the volume of soil that will supply water, and its moisture content. To study this movement a laboratory experiment was set up to measure the amount of water that can be removed from a layer of soil by certain extracting tensions, the rate of extraction, and the zone from which water was removed for certain soils.

The literature dealing with the rate and distance water will move, and the moisture tension range in which it will move, gives conflicting answers. Some workers indicate that the movement is only at low tensions; others believe that movement occurs over the whole range of field moisture. The amount of movement varies from appreciable amounts to very slight (1, 4, 6, 7, 8, 10, 12, and 15).

METHODS AND MATERIALS

The general plan was to moisten a circular mass of soil, 5 cm. deep, and to measure the tension gradients developed in the soil as water was extracted radially through a porous cup in the centre. The soil was

¹ Contribution from Field Husbandry, Soils and Agricultural Engineering Division, Experimental Farms Service, Canada Department of Agriculture, Ottawa, Ont. Based on work done at Swift Current, and submitted as part of a thesis to Utah State University in partial fulfilment of the requirements for the Master of Science degree.

² Research Officer, Field Husbandry Section, Experimental Farm, Swift Current, Sask.

compacted to a uniform density by placing the soil and tanks on a vibrator and shaking for 5 minutes. The soil was supported above the base of the tank on a fine copper screen over expanded metal lath. This allowed a pool of water to be formed under the soil for uniform wetting from the bottom.

The inside of the porous cup at the centre of the circular soil mass was connected to a vacuum system in which the tension was controlled by a thermo cap relay as outlined by Taylor (16). Tensiometers were placed at equally spaced radial intervals from the centre. In early experiments the tensiometers were duplicated and later they were quadruplicated at each distance from the centre. The cups for the tensiometers and the extracting cup were Coors No. 762 filter cups of No. 5 porosity.

Two sizes of tank were used. A tank 90 cm. in diameter was used with soil at zero tension. A tank 30 cm. in diameter was used for soils at higher tensions. This smaller tank had a gypsum plate poured in the bottom to allow the soil to be dried to the desired moisture content by a tension on the bottom.

The soils used were Haverhill loam from near Swift Current, alluvial heavy clay from Rush Lake, and very fine sand from Webb. The soils were passed through a 1-mm. sieve and each was thoroughly mixed to provide a uniform sample.

After the soil, tensiometers and extracting cup were packed in the tray the soil was moistened from below till saturated. For the tests in the large tank the soil was allowed to drain for 24 hours before extraction was started. In the smaller tank tension was applied to the lower surface of the soil to bring it to a tension of about 200 cm. of water. Extraction was started after the soil reached the desired tension, and was done by applying 600 cm. of water suction to the inside of the extracting cup. The amount of water extracted was measured, either by collecting it in a burette or by measuring the rate of movement of water along a calibrated glass tube. At regular time intervals the tensiometers were read and the amount of water extracted was measured.

RESULTS AND DISCUSSION

The tension gradients developed were small and extended over a very short distance from the extracting cup. In most cases no tension gradient could be measured by the tensiometers, even though the tension difference between the inside of the cup and that of the soil was at least 100 cm. of water. The maximum tension gradient measured by the tensiometers was 10 cm. of water tension between the tensiometers 1 cm. from the centre and the ones 9 cm. away. The comparison of these results with those obtained by Richards and Weeks (13) is interesting. In longitudinal horizontal movement they obtained large tension gradients which developed rapidly and extended over several centimetres. The difference can be explained by comparing the radial and longitudinal systems when the radial system has an increasing cross-sectional area for movement to the centre at greater distances from the absorber. In longitudinal movement the cross-sectional area remains constant, whereas in radial movement the cross-section of each succeeding layer farther from the absorber changes rapidly with the radius.

The rise in moisture tension in the soil in all the experiments indicates that water was extracted nearly uniformly from the entire volume of soil. The actual distances that water would move were not determined but under the conditions of this experiment water will move at least 45 cm. in soils at tensions from 0 to 98 cm. of water tension and at least 14 cm. in soils at tensions from 104 to 462 cm. of water tension. This refutes some of the earlier theories that water does not move when soil moisture tensions are greater than 300 cm. of water and indicates that, at least over the range of conditions in this experiment, water will move to a plant root from an appreciable distance.

The change in the soil moisture tension at different distances from the absorber during the extraction period is shown in Tables 1, 2, and 3. Table 1 indicates that water moved from all portions of the soil even at moisture contents below field capacity. The rate of extraction for sand and clay became so low that the experiment was discontinued after tensions of 250 to 270 cm. were reached in the soil. The moisture movement pattern was the same for the three soils at similar moisture tensions.

TABLE 1.—CHANGE IN SOIL MOISTURE TENSION FOR LOAM

Time	Tensiometer readings (cm. water) at different distances (cm.) from extracting cup				
	2	5	8	11	14
hours	cm.	cm.	cm.	cm.	cm.
49.5	298	299	290	294	295
101.0	348	346	341	337	355
155.5	427	428	410	395	414
199.0	460	462	445	434	449
239.5	495	503	474	462	480

TABLE 2.—CHANGE IN SOIL MOISTURE TENSION FOR SAND

Time	Tensiometer readings (cm. water) at different distances (cm.) from extracting cup				
	2	5	8	11	14
hours	cm.	cm.	cm.	cm.	cm.
47.0	104	111	111	119	121
103.0	127	133	132	147	143
150.0	148	150	148	163	163
194.0	170	168	169	189	184
262.5	198	198	204	220	213
343.0	250	250	262	275	265

TABLE 3.—CHANGE IN SOIL MOISTURE TENSION FOR CLAY

Time	Tensiometer readings (cm. water) at different distances (cm.) from extracting cup				
	2	5	8	11	14
hours	cm.	cm.	cm.	cm.	cm.
54.0	213	214	199	201	200
102.0	248	240	225	225	228
146.5	273	272	262	257	270

TABLE 4.—VARIATION IN EXTRACTION RATE WITH CHANGES IN SOIL MOISTURE TENSION (TENSION WAS MEASURED AT TENSIO-METER 5 CM. FROM THE CUP)

Sand		Loam		Clay	
Tension	Rate	Tension	Rate	Tension	Rate
cm. water	ml./hr.	cm. water	ml./hr.	cm. water	ml./hr.
0	33.4	7	44.3	1	22.2
26	12.8	69	1.65	2	1.64
34	1.71	98	1.32	4	0.92
104	0.05	253	0.56	189	0.05
143	0.03	397	0.30	234	0.06
250	0.007	462	0.23	272	0.1

TABLE 5.—RATE OF EXTRACTION PER UNIT GRADIENT

Sand		Loam		Clay	
Soil moisture tension	Rate per unit gradient	Soil moisture tension	Rate per unit gradient	Soil moisture tension	Rate per unit gradient
cm.	ml./hr./cm.(H ₂ O)/cm.	cm.	ml./hr./cm.(H ₂ O)/cm.	cm.	ml./hr./cm.(H ₂ O)/cm.
0	.28	7	.373	1	.185
26	.111	69	.015	2	.013
34	.015	98	.013	4	.0077
104	.0005	253	.008	189	.0006
143	.0003	397	.007	234	.0008
250	.0001	462	.008	272	.0015

The rate of extraction decreased with increased moisture tension as shown in Table 4. In soils at low moisture tension the ratio of the rates for loam-sand-clay were 9 : 5 : 2. In the drier soils this ratio changed to 22 : 2 : 3.

The rate of extraction per unit gradient is shown in Table 5. It is expressed as the rate per hour over the tension gradient per cm. of the first 5 cm. from the absorber.

As the soil became drier the rate of extraction per unit gradient tended to level off. This levelling off is partially due to the reduced gradient in the drier soils as the constant tension was maintained in the cup and the tension of the surrounding soil increased. Thus, the actual gradient was reduced from 600-cm. tension across 5 cm. on wet loam at the beginning of the experiments to 138-cm. tension across the same distance at the end. This reduction in gradient was approximately proportional to the reduction in the rate of extraction to give the levelling off of the extraction rate per unit gradient.

CONCLUSIONS

1. The rate of extraction varied directly with the soil moisture tension.
2. In a horizontal radial system water will move at least 45 cm. in soils at moisture tensions up to 100 cm. of water, and at least 14 cm. in soils with moisture tensions up to 462 cm. of water.

ACKNOWLEDGEMENTS

The author gratefully acknowledges the assistance received from S. A. Taylor, Soil Physicist, Utah State University, Logan, Utah, in initial planning of the experiments and for helpful criticism of this manuscript.

REFERENCES

1. Bouyoucos, G. J. Capillary rise of water in soils under field conditions. *J. Phys. Chem.* 57:45-49. 1953.
2. Briggs, I. J., and J. W. McLane. The moisture equivalents of soils. U.S.D.A. Bureau of Soils Bull. 45. 1907.
3. Buckingham, E. Studies on the movement of soil moisture. U.S.D.A. Bureau of Soils Bull. 38. 1907.
4. Davis, C. H. Adsorption of soil moisture by maize roots. *Botan. Gaz.* 101:791-805. 1940.
5. Day, P. R. The moisture potential of soils. *Soil Sci.* 54:391-400. 1942.
6. Gurr, C. G., T. J. Marshall, and J. T. Hutton. Movement of water in soil due to a temperature gradient. *Soil Sci.* 74:335-345. 1952.
7. Jamison, V. C. Pertinent factors governing the availability of soil moisture to plants. *Soil Sci.* 81:459-471. 1956.
8. Kohnke, H. The practical use of the energy concept of soil moisture. *Soil Sci. Soc. Amer. Proc.* 11:64. 1946.
9. Low, P. F., and J. M. Deming. Movement and equilibrium of water in heterogeneous systems with special reference to soils. *Soil Sci.* 75:187-202. 1953.
10. Marshall, T. J., and C. G. Gurr. Movement of water and chlorides in relatively dry soil. *Soil Sci.* 77:147-152. 1954.
11. Miller, R. D., and F. Richards. Hydraulic gradients during infiltration in soils. *Soil Sci. Soc. Amer. Proc.* 16:33-38. 1952.
12. Richards, L. A., and D. C. Moore. Influence of capillary conductivity and depth of wetting on moisture retention in soil. *Trans. Amer. Geophys. Union* 33:531-540. 1952.
13. Richards, S. J., and L. V. Weeks. Capillary conductivity values from moisture yield and tension measurements on soil columns. *Soil Sci. Soc. Amer. Proc.* 17:206-209. 1953.
14. Russell, M. B. The utility of the energy concept of soil moisture. *Soil Sci. Soc. Amer. Proc.* 7:90-94. 1942.
15. Shaw, B. T. Soil physical conditions and plant growth. *Agronomy* 2:81. 1952.
16. Taylor, S. A. An instrument for controlling pressure, vacuum, and temperature. *Soil Sci.* 79:327-328. 1955.

CHEMICAL, MORPHOLOGICAL AND MINERALOGICAL CHARACTERISTICS OF A CHRONOSEQUENCE OF SOILS ON ALLUVIAL DEPOSITS IN THE NORTHWEST TERRITORIES¹

J. R. WRIGHT, A. LEAHEY AND H. M. RICE

Canada Department of Agriculture, Ottawa, Ontario

[Received for publication October 6, 1958]

ABSTRACT

Three distinct profile types of soil found on alluvial deposits appeared to represent a chronosequence in soil formation. The chemical, morphological and mineralogical characteristics of these soils, classified as Alluvial, Brown Wooded and Grey Wooded, are given and soil development is discussed.

INTRODUCTION

The Grey Wooded soil zone in Canada occupies the forested parts of the Great Plains region in Western Canada as far north as Fort Simpson, Northwest Territories. In the northwestern part of this soil zone three distinct profile types of soil are often found on alluvial deposits. These profile types have been classified as belonging to the Alluvial, the Brown Wooded and the Grey Wooded groups. Usually the Alluvial soil occupies the lowest terrace, the Brown Wooded the middle terraces, and the Grey Wooded the highest terraces above the river. Since the occurrence of these profile types is directly related to their height above the river it would appear that they represent a chronosequence in soil formation.

MATERIALS AND METHODS

The samples of the soils reported on in this paper were collected from sites on a terrace adjacent to and near the mouth of the Hay River in the Northwest Territories. This terrace slopes gently northward parallel to the river and at a somewhat greater gradient than the river. Hence the difference in elevation between the terrace and the stream decreases from south to north. Figure 1 shows the areal soil pattern and the location of the sampling sites. The field work was done during the course of a soil survey along the Mackenzie Highway in the Northwest Territories (3).

Parent Materials

The parent materials of the soils at the three sampling sites consisted of layers of fine textured calcareous alluvium with occasional thin layers of organic matter. While slight differences in texture and in the thickness of the alluvial layers occurred, the parent materials at the three sites appeared to be quite similar.

Vegetation

The soil areas sampled are covered with a heavy stand of mixed woods, dominantly spruce and aspen poplar. Spruce is dominant on the Alluvial soil while aspen is dominant on the Grey Wooded soil.

¹ Joint contribution from Chemistry Division, Science Service (Contribution No. 415), and Field Husbandry, Soils and Agricultural Engineering Division, Experimental Farms Service, Canada Department of Agriculture, Ottawa, Ont.

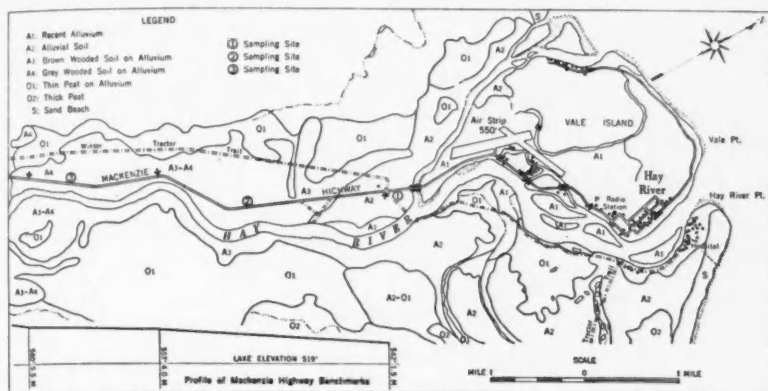


FIGURE 1. Hay River area, showing soil pattern and sampling sites.

Climate

Meteorological records taken at Hay River, a few miles from the sampling sites, give the mean annual temperature as 24° F. and the mean temperature for the 3-month period June, July and August as 55° F. Precipitation is low, averaging 11.8 inches, of which 4.6 inches comes in the form of snow.

Under these vegetative and climatic conditions, the soils are always cool and often dry. In the middle of July, when the soil samples were taken, the temperature at the 6-inch depth in the mineral soil was 42° F., and at 12 inches 40° F., and the soils were dry. These mineral soils do not have a permafrost layer but the subsoils may not completely thaw out until July.

Soils

Alluvial soil: This is a very young well-drained soil, usually found just above the present flood levels of the river. It shows little evidence of profile development, except that free lime has been leached from the upper few inches of the mineral soil. The following is a brief description of the profile sampled:

3 — 0 in. A ₀	: Partly decomposed organic layer	pH 6.4
0 — 3 in. A ₁₁	: Grey (10YR5/1 dry) silty clay loam	pH 6.5
3 — 5 in. A ₁₂	: Greyish brown (10YR5/2 dry) silty clay loam	pH 6.8
5 — 8 in. C ₁	: Dark greyish brown (10YR4/2 dry) silty clay loam, calcareous	pH 8.2
8 — 13 in. C ₂	: Mixed organic and mineral matter, calcareous	pH 8.2
13 — 18 in. C ₃	: Light grey (10YR7/2 dry) silt loam, calcareous	pH 8.4
Friable throughout with weak granular structure		

Brown Wooded soil: This is a well-drained, relatively youthful soil. It shows more development than the Alluvial soil, in that the upper 9 inches are browner in colour, apparently as a result of the loss of organic matter.

Carbonates have also disappeared from this layer. This upper mineral layer often is uniform in colour and structure but occasionally, as in the case of the profile sampled for this study, very weakly developed A₂ and B horizons appear to occur. The following gives a brief description of this profile:

- 3 — 0 in. A₀ : Partly decomposed organic layer pH 6.2
 - 0 — 3 in. A₂ : Greyish brown (10YR5/2 dry) silty clay loam. Weak granular structure pH 6.4
 - 3 — 9 in. B : Brown (10YR4/3 dry) silty clay loam. Weak irregular blocky structure pH 6.5
 - 9 — 14 in. C₁ : Dark greyish brown (10YR4/2 dry) silty clay loam with granular structure pH 8.0
 - 14 — 21 in. C₂ : Pale brown (10YR6/3 dry) silt loam with soft granular structure pH 8.2
- All horizons were friable

Grey Wooded soil: This well-drained soil is the zonal type for the region. It is characterized by an A₀ horizon, a well-developed light coloured A₂ underlain by a darker, finer textured B horizon. The profile sampled for this study is described as follows:

- 2 — 0 in. A₀ : Partly decomposed organic layer with some moss pH 5.1
 - 0 — 4 in. A₂ : Very pale brown (10YR7/3 dry) loam, somewhat platy pH 5.8
 - 4 — 5 in. A/B: Transitional layer—not sampled
 - 5 — 10 in. B₂₁: Pale brown (10YR6/3 dry) clay loam, strong granular structure pH 5.7
 - 10 — 14 in. B₂₂: Yellowish brown (10YR5/6 dry) clay loam, strong granular structure pH 6.0
 - 14 — 17 in. : Mixed partly burnt organic and mineral matter, calcareous, not sampled
 - 17 — 20 in. C : Light yellowish brown (10YR6/4 dry) silt loam, soft granular structure pH 8.4
- All horizons were friable

Investigational Techniques

Samples of the various horizons of each profile were taken by means of a brass cylinder of 275-cc. capacity in order to determine bulk density. The samples were air-dried, ground and passed through a 2-mm. sieve in preparation for physical and chemical analysis. The clay contents of the samples were determined by the hydrometer method of Bouyoucos (1) and the free iron oxide data were obtained by the method described by MacKenzie (4). Iron was determined by reduction with metallic silver and titration with ceric sulphate. Titanium was estimated colorimetrically by the hydrogen peroxide method in a perchloric acid solution. All other methods of analysis used were those given in "Chemical Methods of Soil Analysis" (5).

Samples of the C₂ and C₃ horizons of the Alluvial profile, the C₁ and C₂ horizons of the Brown Wooded profile and the B₂₂ and C horizons of the Grey Wooded profile were examined mineralogically. The sand was separated into three specific gravity groups and representative samples

TABLE 1.—SELECTED PHYSICAL AND CHEMICAL ANALYSES OF THREE SOIL PROFILES

Horizon	Depth	pH	CaCO ₃ ¹	Organic ¹ matter	N ¹	C/N ratio	Clay ¹	Bulk density	"Free" ^{1,2} Fe ₂ O ₃	"Free"/Total iron
	in.		%	%	%		%		%	%
ALLUVIAL										
A ₀	3-0	6.4	—	85.8	1.63	30.5	—	0.11	—	—
A ₁	0-3	6.5	0.0	9.2	0.30	17.8	40	0.74	2.62	55.8
A ₂	3-5	6.8	0.0	5.7	0.21	15.8	40	0.81	2.84	55.6
C ₁	5-8	8.2	14.8	7.7	0.34	13.2	33	0.86	1.79	44.8
C ₂	8-13	8.2	18.4	6.1	0.27	13.1	—	0.98	1.98	47.9
C ₃	13-18	8.4	17.5	3.0	0.13	13.4	—	1.22	1.98	45.6
BROWN WOODDED										
A ₀	3-0	6.2	—	81.4	1.84	25.7	—	0.10	—	—
A ₂	0-3	6.4	0.0	4.1	0.18	13.2	39	0.97	2.92	57.6
B	3-9	6.5	0.0	3.2	0.12	15.4	37	1.16	2.90	56.0
C ₁	9-14	8.0	6.7	7.2	0.32	13.1	—	1.10	2.40	55.1
C ₂	14-21	8.2	14.4	1.8	0.09	11.7	27	1.33	2.05	51.3
GREY WOODDED										
A ₀	2-0	5.1	—	73.3	1.53	27.8	—	0.09	—	—
A ₂	0-4	5.8	0.0	1.4	0.07	11.6	18	1.14	1.86	52.1
B ₁	5-10	5.7	0.0	1.0	0.09	6.5	35	1.43	2.57	55.2
B ₂	10-14	6.0	0.0	0.8	0.06	7.7	35	1.47	3.16	65.7
C	17-20	8.4	15.4	1.4	0.07	11.6	24	1.36	1.93	56.6

¹ Data expressed on a moisture-free basis² "Free" iron oxide removed from the soil by MacKenzie's sodium hydrosulphite method

TABLE 2.—TOTAL CHEMICAL ANALYSES OF THREE SOIL PROFILES
(Data expressed on a moisture-free basis)

Horizon	Depth in.	Loss on ignition %	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	TiO ₂ %	CaO %	MgO %	K ₂ O %	Na ₂ O %	P ₂ O ₅ %	Total %
ALLUVIAL												
A ₁₁	0-3	14.32	61.34	13.81	4.70	0.70	1.47	1.57	2.02	0.53	0.14	100.60
A ₁₂	3-5	10.73	63.78	14.52	5.11	0.72	1.26	1.64	2.24	0.51	0.11	100.62
C ₁	5-8	17.94	54.24	9.82	4.00	0.50	8.82	1.81	1.90	0.50	0.18	99.71
C ₂	8-13	17.93	52.09	9.78	4.14	0.52	10.66	2.04	1.92	0.47	0.14	99.69
C ₃	13-18	14.05	55.05	10.90	4.35	0.59	9.33	2.34	2.23	0.47	0.16	99.47
BROWN WOODED												
A ₂	0-3	8.28	67.85	13.57	5.07	0.74	0.98	1.43	2.34	0.60	0.13	100.99
B ₁	3-9	7.21	68.61	13.21	5.18	0.71	0.98	1.53	2.25	0.57	0.10	100.35
C ₁	9-14	13.60	60.93	11.18	4.36	0.52	4.56	1.72	2.18	0.52	0.16	99.73
C ₂	14-21	10.73	62.63	9.32	4.00	0.57	7.55	2.20	1.86	0.60	0.16	99.62
GREY WOODED												
A ₂	0-4	3.78	79.34	8.93	3.57	0.61	0.54	0.85	1.77	0.69	0.14	100.22
B ₂₁	5-10	4.41	73.54	12.54	4.66	0.62	0.59	1.27	2.20	0.66	0.10	100.59
B ₂₂	10-14	4.43	72.74	12.17	4.81	0.58	0.78	1.25	2.08	0.63	0.12	99.59
C	17-20	9.96	65.72	8.44	3.41	0.48	7.58	1.92	1.52	0.63	0.16	99.82

were examined by means of a petrographic microscope, a minimum of 300 grains in each being identified. The silt and clay fractions (coarse, medium, and fine) were examined with a Norelco x-ray diffractometer using Ni-filtered Cu K_α radiation. The general procedure was similar to that used in most clay mineralogy laboratories.

RESULTS AND DISCUSSION

It seems pertinent at this point to restate the general equation of soil formation:

Soil = f (climate, vegetation, soil drainage, parent material, time).

In the development of these soils, the soil-forming factors—climate, vegetation, soil drainage and parent material—appeared to be relatively constant, while time was the variable.

Data obtained from selected physical and chemical analyses are shown in Table 1. The disappearance of carbonates and accompanying fall in pH as a function of depth indicate the chronological order of these profiles to be Alluvial, Brown Wooded, and Grey Wooded, and thus support the order of maturity of these profiles as indicated by field observations.

The Alluvial and Brown Wooded profiles are well supplied with organic matter, while the Grey Wooded is low in this constituent. The loss of organic matter in the profiles is associated with the removal of carbonates. Both the organic matter content and the C/N ratio decrease in the soils with increasing age of the soils.

There is no evidence of translocation of clay in the Alluvial and Brown Wooded profiles. In the Grey Wooded profile, however, the clay content is highest in the B horizon, indicating significant eluviation of clay from the A and its accumulation in the B horizon. Values for bulk density also attain a maximum in the B, possibly because of clay moving into voids in this horizon resulting in an increase in weight without concomitant increase in volume.

The effects of the podzolization process(es) become quite evident in the Grey Wooded profile. In the younger profiles the values for "free" iron, expressed as per cent of the total iron, are higher in the upper parts of the profiles, indicating mainly *in situ* deposition rather than translocation of this element. In the Grey Wooded profile, however, values of 52.1, 65.7 and 56.6 for the A₂, B₂₂ and C horizons, respectively, show significant translocation of iron. Similarly, the data for total Fe_2O_3 and Al_2O_3 , given in Table 2, show a pronounced sesquioxide bulge in the B horizon of the Grey Wooded profile, even when the data for the C horizon are recalculated on a carbonate-free basis.

Total chemical analyses of the various mineral horizons of the profiles are recorded in Table 2. Such detailed and complete analyses on the chemical composition of soils of this region were not previously available. Further interpretation of these data was done by utilizing molecular values which give a clearer picture of stoichiometric relationships than do weight data. Furthermore, ratios of these values eliminate the effects of additions of organic matter, losses of carbonates, etc., and thus afford a method of detecting relative translocations of elements.

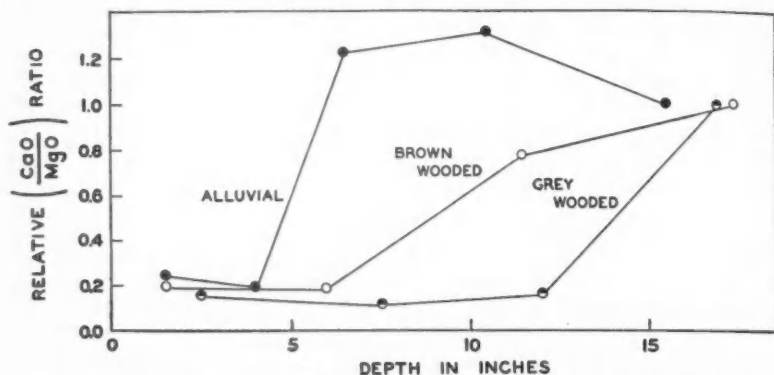


FIGURE 2. The relative ratio of calcium oxide to magnesium oxide plotted as a function of depth for three profiles.

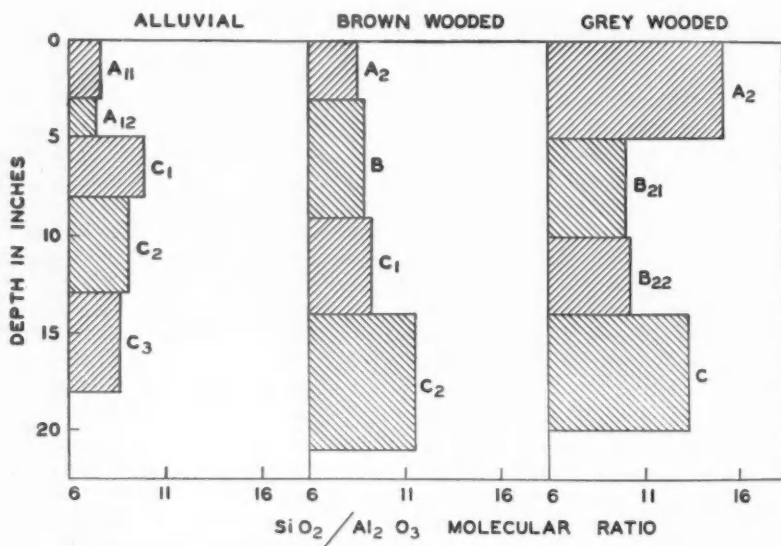


FIGURE 3. Molecular ratios of silica to alumina of horizons in profiles forming a chronosequence.

Figure 2 shows the relative molecular ratios of CaO to MgO plotted as a function of depth with the ratio of the lowest horizon of each profile set at unity. The curves show that calcium is more readily leached from these materials than is magnesium. From the $\text{CaO}/\text{Al}_2\text{O}_3$ and $\text{MgO}/\text{Al}_2\text{O}_3$ data of molecular ratios presented in Table 3, it is apparent that approximately 90 per cent of the calcium compared with 50 per cent of the magnesium has been removed from the parent materials during the development of the sola of these profiles.

TABLE 3.—MOLECULAR RATIOS CALCULATED FROM TOTAL CHEMICAL ANALYSES DATA

Horizon	SiO ₂		CaO		MgO		Na ₂ O		K ₂ O		K ₂ O	
	Al ₂ O ₃ + Fe ₂ O ₃		Al ₂ O ₃		Al ₂ O ₃		Al ₂ O ₃		Al ₂ O ₃		Al ₂ O ₃	
	Abs. ¹	Rel. ²	Abs.	Rel.	Abs.	Rel.	Abs.	Rel.	Abs.	Rel.	Abs.	Rel.
ALLUVIAL												
Au	6.20	0.91	0.19	0.12	0.29	0.53	0.06	0.89	0.16	0.72	2.51	0.80
A ₁₂	6.10	0.89	0.16	0.10	0.29	0.53	0.06	0.82	0.17	0.75	2.90	0.93
C ₁	7.45	1.09	1.64	1.05	0.47	0.86	0.08	1.18	0.21	0.95	2.51	0.80
C ₂	7.13	1.04	1.99	1.27	0.53	0.97	0.08	1.12	0.21	0.96	2.70	0.86
C ₃	6.84	1.00	1.56	1.00	0.55	1.00	0.07	1.00	0.22	1.00	3.13	1.00
BROWN WOODDED												
A ₃	6.86	0.77	0.13	0.09	0.27	0.45	0.07	0.69	0.19	0.86	2.57	1.26
B	7.06	0.79	0.14	0.09	0.30	0.49	0.07	0.67	0.18	0.85	2.61	1.27
C ₁	7.42	0.83	0.74	0.50	0.39	0.65	0.08	0.72	0.21	0.98	2.76	1.35
C ₂	8.97	1.00	1.48	1.00	0.60	1.00	0.11	1.00	0.22	1.00	2.04	1.00
GREY WOODDED												
A ₂	12.04	1.14	0.11	0.07	0.24	0.42	0.13	1.02	0.21	1.10	1.72	1.08
B ₂₁	8.06	0.77	0.09	0.05	0.26	0.45	0.09	0.71	0.19	0.97	2.20	1.38
B ₂₂	8.12	0.77	0.12	0.07	0.26	0.45	0.09	0.69	0.19	0.95	2.18	1.37
C	10.53	1.00	1.64	1.00	0.58	1.00	0.12	1.00	0.20	1.00	1.59	1.00

¹ Absolute ratios² Relative ratios based on the lowest horizon as unity

TABLE 4.—MINERALS OF THE SAND FRACTIONS
(as per cent of sand)

Sample	Total sand ¹	Quartz	Feldspars		Micas	Garnets	Titanium minerals ²				Topaz	Tourmaline	Zircon	Others
			Total	Weathered			Ilmenite	Brookite	Rutile	Titanite				
Alluvial	1.6	2.9	73.2	7.7	4.8	—	0.28	—	0.01	—	0.03	0.03	—	18.8
C ₃	0.7	1.8	69.3	6.5	8.4	0.8	0.29	—	0.02	0.03	0.01	0.03	0.01	19.3
Brown	7.1	10.7	63.2	10.4	7.4	0.1	0.31	—	0.11	0.03	0.05	0.02	—	18.1
Wooded	20.0	6.7	61.5	14.9	2.9	0.2	0.15	—	0.01	—	0.02	0.07	0.01	28.4
C ₂	22.9	9.3	67.8	11.6	2.1	0.2	0.08	—	0.04	0.04	0.01	0.04	—	20.4
Grey	23.3	25.7	50.3	18.5	3.2	0.3	0.03	0.05	0.03	—	—	0.05	—	20.3
Wooded														
C														

¹ As per cent of moisture-free, salt-free and organic matter-free sample

Silica-alumina ratios for the three profiles are shown in Figure 3. Comparing the youngest (Alluvial) with the oldest (Grey Wooded) profile, there is a marked decrease in alumina with respect to silica in the A horizons with time. However, these ratios and the $\text{SiO}_2/\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ relative ratios given in Table 3 indicate that in the earlier stages of development (Alluvial and Brown Wooded) there have been greater losses of silica relative to sesquioxides in the sola. In the next stage in the development of these soils, exemplified by the Grey Wooded profile, the significantly higher silica-sesquioxide ratios for the A horizon reflect greater leaching of the sesquioxides with respect to silica. Apparently, after depletion of carbonates, a further modification of the soil material occurred before significant translocation of sesquioxides took place. Thus, with continued loss of bases, particularly calcium, and accompanying decrease in pH from 6.4 in the A horizon of the Brown Wooded to 5.8 in the A horizon of the Grey Wooded soil, marked losses of sesquioxides relative to silica have occurred.

Jenny (2) has pointed out that potassium and sodium are particularly sensitive criteria of leaching intensities as a result of weathering and soil formation. Although the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratios given in Table 3 show some leaching of sodium and potassium, it is apparent that

TABLE 5.—MINERALS OF THE SILT FRACTIONS

Sample		Quartz	Feldspars	Micas and Illite	Chlorite	Kaolinite
Alluvial						
C ₂	Coarse ¹	+++	+	—	—	—
	Medium ²	+++	+	+	+	+
	Fine ³	++	+	+	+	+
C ₃	Coarse	+++	+	—	—	—
	Medium	+++	+	+	+	+
	Fine	++	+	+	+	+
Brown Wooded						
C ₁	Coarse	+++	+	tr.	+	—
	Medium	+++	+	++	+	+
	Fine	++	+	+	+	+
C ₂	Coarse	+++	+	tr.	+	—
	Medium	+++	+	+	+	+
	Fine	++	+	+	+	+
Grey Wooded						
B ₂₂	Coarse	+++	+	+	tr.	—
	Medium	+++	+	+	+	+
	Fine	++	—	+	+	+
C	Coarse	+++	+	+	tr.	tr.
	Medium	+++	+	+	+	+
	Fine	++	—	+	+	+

¹ Coarse silt..... 50–20 μ ² Medium silt..... 20– 5 μ ³ Fine silt..... 5– 2 μ +++ strong pattern
++ moderate pattern
+ weak pattern
tr. pattern barely perceptible

TABLE 6.—MINERALS OF THE CLAY FRACTIONS

Sample		Quartz	Illite	Montmorillonite	Chlorite	Kaolinite	Mixed layer
Alluvial							
C ₂	Coarse ¹	++	++	tr.	+	+	+
	Medium ²	—	+++	tr.	tr.	+	++
	Fine ³	—	++	—	—	tr.	+++
C ₃	Coarse	++	++	tr.	+	+	+
	Medium	—	++	—	—	tr.	++
	Fine	—	++	+	—	tr.	++
Brown Wooded							
C ¹	Coarse	++	++	tr.	tr.	+	+
	Medium	tr.	++	tr.	—	tr.	++
	Fine	—	++	+	—	+	++
C ₂	Coarse	++	++	tr.	+	+	+
	Medium	—	++	tr.	—	+	++
	Fine	—	+	+	—	tr.	+++
Grey Wooded							
B ₂₂	Coarse	++	++	tr.	tr.	+	+
	Medium	—	++	+	—	+	+++
	Fine	—	++	+	—	tr.	+++
C	Coarse	++	++	+	tr.	+	+
	Medium	—	++	tr.	—	+	++
	Fine	—	++	+	—	—	++

¹ Coarse clay.....2.0-0.2 μ ² Medium clay.....0.2-0.1 μ ³ Fine clay.....<0.1 μ +++ strong pattern
++ moderate pattern
+ weak pattern
tr. pattern barely perceptible

chemical alterations within the profiles as regards these elements are not very profound. The trends of the K₂O/Na₂O molecular ratios, given in Table 3, do indicate greater loss of sodium than potassium with age, reflecting a greater degree of weathering.

The results of mineralogical analyses are presented in Tables 4, 5 and 6 for the sands, silts and clays respectively. In the sands, the quartz content was lowest in the Alluvial soil and highest in the Grey Wooded C sample. The quartz grains in the latter were clear, oval and highly polished with no sharp edges, probably the result of considerable resorbing in water. The most prevalent mineral group was the feldspars. Weathered feldspars were present in greatest amount in the Grey Wooded C horizon. Garnets were most numerous in the Alluvial C₃ sample. Many of the garnets in the Grey Wooded horizons showed considerable strain and incipient weathering to epidote, indicating that they had probably passed through several weathering cycles. Four titanium minerals were identified. The grains of brookite in the C horizon of the Grey Wooded profile were the first of this type to be identified in these laboratories.

In the silts, the distribution of all minerals identified was relatively uniform among all samples. Quartz was predominant and was slightly lower in amount in the fine than in the medium and coarse fractions.

The clay mineral components of the medium and fine clay fractions were largely illite and a mixed-layer complex of illite and montmorillonite. The coarse clays had an appreciable amount of quartz and less mixed-layer material.

The mineralogical composition of the silts and clays is very similar among the C horizons of the three profiles. As far as the sand fractions are concerned, differences demonstrate the variability that can be expected in alluvial deposits. The sands have probably been transported relatively short distances and hence might be considered as derived from local sources. The silts and clays are more likely to have been carried over greater distances and thoroughly mixed in the process.

CONCLUSIONS

The present studies indicate that the pattern of development in the formation of these soils on calcareous alluvial materials in Northwestern Canada is as follows:

1. Accumulation of organic matter in the upper part of the calcareous soil-forming materials. Occurrence of high organic layers in the sub-soils is attributed to burial by alluvium during the build-up of the parent materials.
2. Decomposition of carbonates, with calcium being removed about twice as rapidly as magnesium, followed by the depletion of organic matter.
3. Greater loss of silica than sesquioxides in the earlier stages of development probably during depletion of carbonates.
4. Continued loss of bases, particularly calcium, subsequent to depletion of carbonates accompanied by a further decrease in pH and further loss of organic matter.
5. Marked eluviation of clay and accelerated leaching of iron and aluminium with respect to silica resulting in a distinct siliceous eluviated layer (A₂) underlain by a clay- and sesquioxide-enriched layer (B).

ACKNOWLEDGEMENT

The authors wish to thank R. Levick for making the total chemical analysis, and L. M. Patry for the petrographic analysis.

REFERENCES

1. Bouyoucos, G. J. A recalibration of the hydrometer method for making mechanical analysis of soils. *J. Amer. Soc. Agron.* 43:434-438. 1951.
2. Jenny, H. *Factors of soil formation*. McGraw-Hill Book Co., New York, N. Y. 1941.
3. Leahey, A. Preliminary soil survey of lands adjacent to the MacKenzie Highway in the Northwest Territories. Mimeo. Rept., Can. Dept. Agr., Ottawa. 1953.
4. MacKenzie, R. C. Free iron-oxide removal from soils. *J. Soil Sci.* 5:167-172. 1954.
5. Wright, L. E., *et al.* Chemical methods of soil analysis. Chem. Div., Sci. Service, Can. Dept. Agr., Ottawa. 1949.

ALKALINE PERMANGANATE OXIDATION OF THE ORGANIC MATTER OF THE A₀ AND B₂₁ HORIZONS OF A PODZOL¹

J. R. WRIGHT AND M. SCHNITZER

Canada Department of Agriculture, Ottawa

[Received for publication October 29, 1958]

ABSTRACT

The organic matter of the A₀ and B₂₁ horizons of a podzol soil has been oxidized with alkaline permanganate under conditions similar to those employed by Bone *et al.* (1,2). Using a slight excess of alkaline permanganate, about 65 per cent of the carbon of the A₀ horizon was oxidized to CO₂, 23 per cent to oxalic acid and 2 per cent to acetic acid. The remaining 10 per cent resisted oxidation to these products. Under the same conditions 92 per cent of the carbon of the B₂₁ horizon was oxidized to CO₂, 7 per cent to oxalic acid and 1 per cent to acetic acid.

In order to obtain additional identifiable products less drastic conditions were used. The organic matter of the A₀ horizon was oxidized at a KMnO₄/organic matter ratio of 4.7-1 and that of the B₂₁ horizon at ratios of 2.5-1 and 5.0-1.

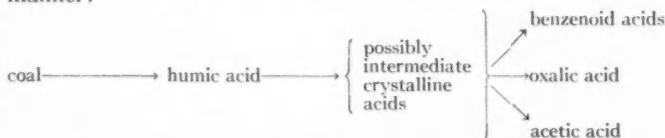
The products of oxidation were fractionated by the scheme of Bone *et al.* (1). While the mean composition of a substantial portion of the CO₂-free oxidation products approximated to that of benzene di- and tricarboxylic acids and that of another fraction to saturated open chain acids, numerous attempts to isolate these acids in pure forms were unsuccessful. Reasons for the failure to isolate these acids are advanced.

INTRODUCTION

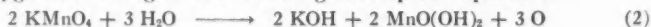
It has long been recognized that there is a close connection between the movement of sesquioxides and that of organic matter in the development of podzol soils. The mechanism involved remains obscure, mainly because little is known about the chemical constitution of the organic material(s) moving through the A₂ and into the B horizon of the profile.

The object of this investigation was to study the controlled oxidation in alkaline permanganate solution of the organic matter occurring in the A₀ and B₂₁ horizons of a podzol soil.

A considerable amount of work has been done on the alkaline permanganate oxidation of coal and related substances. Bone *et al.* (1) view the alkaline permanganate oxidation of coal to occur in the following manner:



The oxidation normally proceeds as a result of the liberation of available oxygen according to the following incomplete equation:



Bone *et al.* (1) made a quantitative study of the oxidation products from cellulose, lignin, peat, lignite, bituminous and anthracite coals treated with alkaline permanganate. In the case of coals, benzenoid acids were

¹ Contribution No. 417, Chemistry Division, Science Service, Canada Department of Agriculture.

obtained in yields up to 50 per cent, which led them to state that "in great part the coal substance has an essentially benzenoid structure". With peat, 10 to 25 per cent of the carbon appeared as benzenoid acids. Recently, Piret *et al.* (4), confirming Bone's results, reported that alkaline permanganate solution converted 13 to 22 per cent of the carbon of peat to water-soluble aromatic polycarboxylic acids.

As a part of the investigation reported herein it was of interest to identify the oxidation products, especially benzene carboxylic acids, resulting from the alkaline permanganate oxidation of the organic matter of the A₀ and B₂₁ horizons. It was hoped that such a study would shed some light on the chemical structure of the organic matter.

MATERIALS AND METHODS

The soil samples came from the A₀ and B₂₁ horizons of the Armadale profile (5), an imperfectly drained podzol from Prince Edward Island. The analytical methods used to establish the carbon balance were essentially those described by Bone *et al.* (1). A given weight of soil (5g. of A₀ and 50g. of B₂₁ material), suspended in KOH solution so as to give a KOH to organic matter (Cx 1.724) ratio of 1.6, was oxidized with 3 per cent permanganate solution added slowly from a dropping funnel. The apparatus used was that described by Piret *et al.* (4). The volumes of permanganate solution added were adjusted to give the desired KMnO₄/organic matter ratios. When necessary, distilled water was added to make a final volume of about 1000-1200 ml. The operation started at about 70°C., but was chiefly conducted at the boiling point of the medium at atmospheric pressure. Except where an excess of permanganate was used, the operation was continued for 2 hours beyond the disappearance of the pink colour. The total reaction time was 4 to 5 hours. Where an excess of permanganate was used the reaction was allowed to proceed for 6 hours in order to obtain maximum oxidation under these experimental conditions. At the end of this period the mixture was cooled and filtered to remove the precipitated manganese dioxide and the residual soil. After washing the residue, the combined filtrate and washings were analysed for four types of carbon compounds—carbonate carbon, volatile acids, oxalic acid and residual or higher acids. The yield of the latter was estimated from the difference between total carbon and the sum of the other three types of carbon. Volatile acids, calculated as acetic acid, were determined by distilling an aliquot acidified with dilute sulphuric acid followed by titration of the distillate. Oxalate was precipitated as calcium oxalate, which was then dissolved in hot dilute sulphuric acid and titrated with standard permanganate solution. Total and carbonate carbon were measured manometrically according to Van Slyke and Folch (7), and Bremner (3), respectively. Ultimate analysis for carbon and hydrogen were done by dry combustion, and nitrogen by micro-Kjeldahl. Electrodialysis was carried out in a 3-cell Mattson-type apparatus at a maximum current of 250-300 milliamps. All evaporations were done under vacuum at room temperature.

RESULTS

Carbon Balance

Before making a more detailed study of the oxidation products it was important, first of all, to determine the relative proportions of KMnO_4 /organic matter to be used in order to obtain possible identifiable products aside from CO_2 and water.

Figures 1 and 2 show the distribution into volatile, oxalate, carbonate and residual carbon with increasing KMnO_4 /organic matter ratios for the A_0 and B_{21} horizons. These ratios were increased until an excess permanganate solution, as indicated by a permanent pink colour, had been added. The ratios at this stage were approximately 8 for the A_0 and 6 for the B_{21} material. Both figures show a rapid decrease in the residual (resistant to oxidation) carbon with increasing KMnO_4 /organic matter ratios. Simultaneously, there was a rapid increase in carbonate carbon and to a certain extent in oxalate carbon, the latter depending on the source of the organic matter. At low ratios the main oxidation product was CO_2 . With higher ratios increased amounts of oxalic acid were produced along with CO_2 . With further increasing ratios even the oxalate or at least portions of it were oxidized to CO_2 as indicated by the sharp rise and fall in the carbonate and oxalate curves respectively. With sufficiently high ratios to give an excess of permanganate, almost 100 per cent of the carbon of the B_{21} and approximately 90 per cent of that of the A_0 horizons could be oxidized to CO_2 and oxalic acid.

Fractionation of CO_2 -free Oxidation Products

After having established the carbon balance, intermediate KMnO_4 /organic matter ratios were selected for a more detailed investigation of the oxidation products. A 4.7:1 ratio was selected for the A_0 material while the B_{21} material was oxidized at ratios of 2.5:1 and 5:1. Following oxidation, the products were electrodialyzed (the pH dropped to less than 2) and fractionated according to the scheme shown in Figure 3.

Table 1 gives a number of characteristics for each fraction. Although the NH_4OH -insoluble fractions consisted predominantly of oxalic acid, appreciable amounts of this acid occurred in the NH_4OH - and H_2O -soluble fractions. No oxalic acid was present in the acetone-soluble fractions. About one-half of the total yield of oxidation products of the A_0 material was oxalic acid. In the case of the B_{21} horizon, as the ratio of KMnO_4 /organic matter increased from 2.5:1 to 5:1, the yield of oxalic acid in the fractions increased from 28 to 47 per cent. Probably the most important fraction was the NH_4OH -soluble material which constituted in all cases approximately 50 per cent of the oxalate-free organic matter. The presence of oxalic acid in the NH_4OH -insoluble fractions was verified by esterification and vacuum distillation of the resulting dimethyl ester, the melting point of which agreed closely with that reported in the literature (found 53°C ., theoretical 54°C .). An additional check was made by forming the calcium salt and analysing for calcium (found 27.15 per cent, theoretical 27.43 per cent).

The NH_4OH -insoluble fraction of the oxidation products of the A_0 material contained 60 per cent oxalic acid. Since investigations on coal (1) and peat (4) had established the presence of substantial amounts of

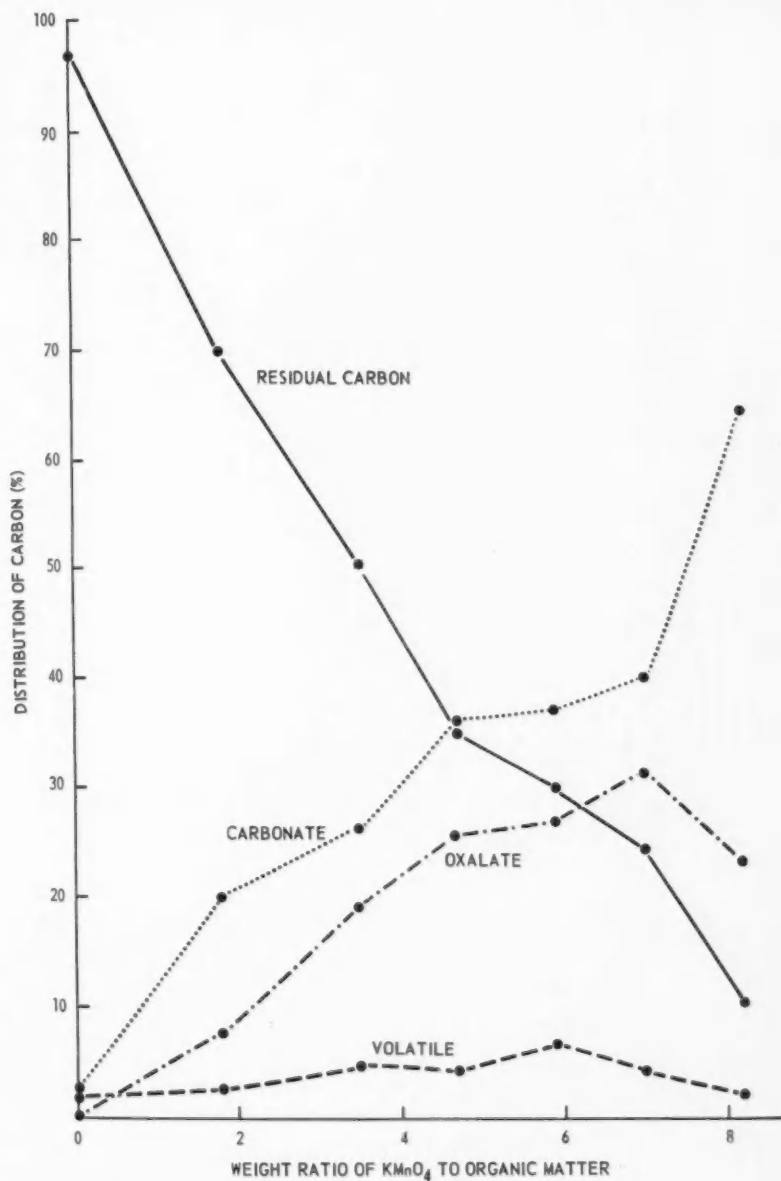


FIGURE 1. Effect of potassium permanganate-organic matter ratio on carbon distribution of the A_0 horizon.

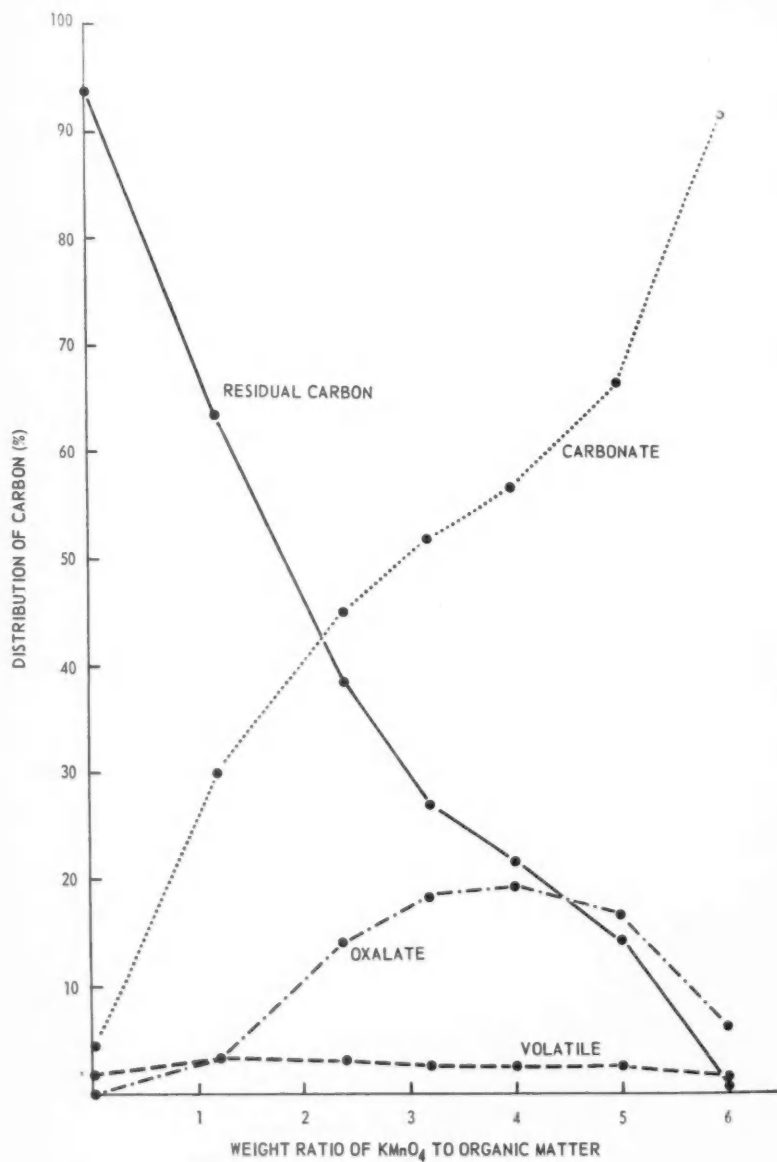


FIGURE 2. Effect of potassium permanganate-organic matter ratio on carbon distribution of the B_{21} horizon.

TABLE 1.—ANALYTICAL CHARACTERISTICS OF FRACTIONS OBTAINED FOLLOWING ALKALINE PERMANGANATE OXIDATION OF THE ORGANIC MATTER OF THE A₀ AND B₂₁ HORIZONS

	Yield C %	Yield ¹ C %	C ¹ %	H ¹ %	O ¹ %	N ¹ %	C/H	O/H
A ₀ (4.7:1)								
Acetone sol.	2	2	46.9	4.1	48.0	1.0	11.4	11.7
NH ₄ OH sol.	29	25	52.1 ²	3.3 ²	42.5 ²	2.1 ²	15.8	12.9
NH ₄ OH insol.	66	26	Mainly oxalic acid					
H ₂ O sol.	3	?	36.2	4.2	57.6	2.0	8.6	13.7
		55						
(Oxalic acid by diff. 45)								
B ₂₁ (2.5:1)								
Acetone sol.	13	13	54.1	4.2	40.4	1.3	12.9	9.6
NH ₄ OH sol.	47	35	58.6 ²	3.2 ²	36.4 ²	1.8 ²	18.3	11.4
NH ₄ OH insol.	10	0	All oxalic acid					
H ₂ O sol.	30	24	44.9	3.9	49.9	1.3	11.5	12.8
		72						
(Oxalic acid by diff. 28)								
B ₂₁ (5:1)								
Acetone sol.	3	3	51.6	4.1	43.3	1.0	12.6	10.6
NH ₄ OH sol.	36	32	51.9 ²	3.5 ²	42.4 ²	2.2 ²	14.8	12.1
NH ₄ OH insol.	38	0	All oxalic acid					
H ₂ O sol.	23	18	40.2	3.5	53.3	3.0	11.5	15.2
		53						
(Oxalic acid by diff. 47)								

¹ Oxalic acid-free² Oxalic acid- and ammonia-free

mellitic acid in this fraction, it was thought that the remaining 40 per cent might contain mellitic acid. Numerous attempts by esterification and vacuum distillation, solvent-solvent extraction and chromatographic techniques failed to establish the presence of appreciable amounts of this acid.

DISCUSSION

A comparison of Figures 1 and 2 indicates that the organic matter of the A₀ was more resistant to alkaline permanganate oxidation than that of the B₂₁ horizon. It required KMnO₄/organic matter ratios of 8 and 6 respectively to give an excess of permanganate. Under the same conditions, 90 to 100 per cent of the carbon was oxidized chiefly to CO₂ and in some degree to oxalic acid. In this regard soil organic matter differs significantly from coal. Bone *et al.* (2) determined the carbon balance of the products resulting from the oxidation of cellulose, lignins, peats, brown coals, bituminous coals and anthracites, using a slight excess of alkaline permanganate. Cellulose yielded no benzene carboxylic acids while lignins, peats, brown coals, bituminous coals and anthracites produced 12-16, 10-25, 22-34, 39-46 and 50 per cent respectively. Yields of oxalic acid were 49 per cent for cellulose and 21-22, 15-28, 9-23, 13-14 and 7 per cent for the other substances. Assuming that the residual carbon fraction of the A₀ horizon

TABLE 2.—COMPOSITION OF A NUMBER OF AROMATIC AND ALIPHATIC CARBOXYLIC ACIDS

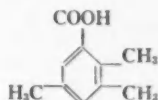
Acid	C %	H %	O %	Ratio C H	Ratio O H
Benzene carboxylic	68.8	5.0	26.2	14	5.2
Benzene dicarboxylic	57.8	3.6	38.5	16	10.7
Benzene tricarboxylic	51.4	2.9	45.7	18	16
Benzene tetracarboxylic	47.3	2.4	50.4	20	21.3
Benzene pentacarboxylic	44.3	2.0	53.7	22	26.7
Benzene hexacarboxylic	42.1	1.8	56.2	24	32
Oxalic	26.7	2.2	71.1	12	32
Succinic	40.7	5.1	33.2	8	10.3
Glutaric	45.5	6.1	48.4	7.5	8
Adipic	49.3	6.4	44.3	7.2	6.4
Azelaic	52.5	7.5	40.0	7.0	5.3
Suberic	55.2	8.1	36.7	6.9	4.6
CH ₂ .COOH propane CH ₂ .COOH tricarboxylic	40.9	4.5	54.5	9	12
CH ₂ .COOH butane (CH ₂ .COOH) ₂ tetracarboxylic	41.0	4.3	54.7	9.6	13
CH ₂ .COOH pentane (CH ₂ .COOH) ₂ pentacarboxylic	41.1	4.1	54.8	10	13.3
CH ₂ .COOH hexane (CH ₂ .COOH) ₄ hexacarboxylic	41.1	4.0	54.9	10.3	13.5
CH ₂ .COOH heptane (CH ₂ .COOH) ₅ heptacarboxylic	41.2	3.9	54.9	10.5	14.0
CH ₂ .COOH octane (CH ₂ .COOH) ₆ octacarboxylic	41.2	3.9	54.9	10.7	14.2

oxidized under the same conditions consisted mainly of benzene carboxylic acids, in this respect this type of organic matter behaved similar to lignin and peat. Similarities in the yields of oxalic acid further support this view.

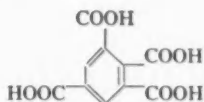
When the analytical data of Table 1 are compared with those of Table 2, which show the composition of a number of carboxylic acids, it can be seen that the mean composition of the NH₄OH-soluble fractions approximated that of benzene di- and tri-carboxylic acids. The H₂O-soluble fractions more nearly corresponded to the saturated open chain acids.

Bone *et al.* (1,2) have carried out alkaline permanganate oxidations of a number of aromatic substances under conditions comparable with those of this investigation. The information thus obtained should be helpful in interpreting the results of this study.

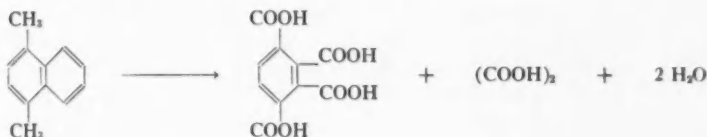
For example, (a) 2,3,5-trimethylbenzoic acid,



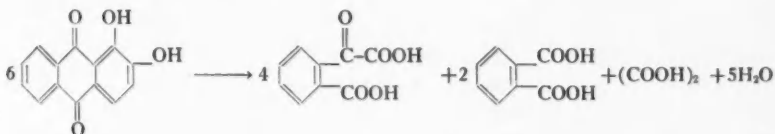
was slowly oxidized chiefly to 1,2,3,5-benzenetetracarboxylic acid,



(b) 1,4-dimethylnaphthalene was slowly oxidized to 1,2,3,4-benzenetetracarboxylic and oxalic acids, presumably thus:

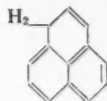
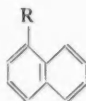


(c) 1,2-dihydroxy-anthraquinone. The introduction of two hydroxy groups into the anthraquinone molecule greatly facilitated its oxidation with the production of phthalonic, phthalic and oxalic acids in substantially the following molecular proportions:



According to Bone *et al.* (1,2) it is not difficult to account for the production of benzene carboxylic acids by the alkaline permanganate oxidation of coal or humic acid.

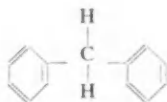
Thus a 1,2,3-benzenetricarboxylic acid, for example, would result either from such fused rings as,



where R = side chain, while 1,3,4-benzenetricarboxylic acid might result from



It would also be possible for benzene carboxylic acids to arise by oxidation of such structures as



Mellitic (benzenhexacarboxylic) acid would arise from the oxidation of fused ring structures such as the following:



Indeed, the production of any benzene carboxylic acid might be explained on similar lines.

Oxalic acid might arise simultaneously by the oxidation of benzene rings and/or alkyl side chains, while acetic acid obviously would result from the oxidation of side chains.

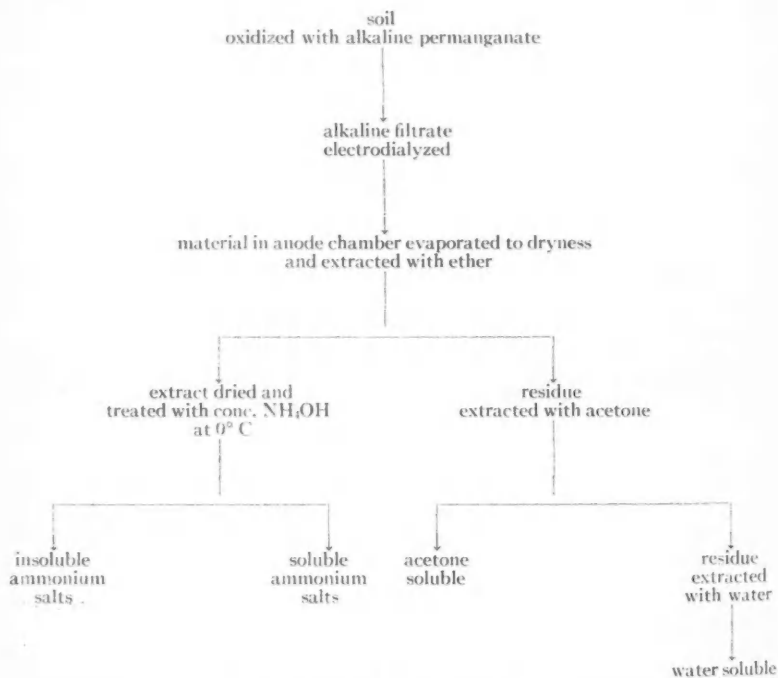


Figure 3. Fractionation scheme.

In this investigation, however, numerous attempts to isolate pure di- and tri-carboxylic acids in significant amounts were not successful. The absence of mellitic acid in the oxidation products indicates that the original organic matter of both horizons did not contain such complex fused benzenoid ring structures as mentioned earlier. Evidence that these fractions contained carboxyl groups was obtained by infra-red spectroscopy, rapid migration to the positive pole on electrodialysis, ready formation of silver and barium salts and considerable titratable acidity below pH 8. Failure to isolate and identify appreciable amounts of pure benzene carboxylic acids means that either these acids were still present in more complex or polymerized forms, or indeed not present at all. The absence of identifiable benzene carboxylic acids in the oxidation products does not necessarily mean that benzenoid ring structures were not present in the original soil organic matter. It is known (2) that substitution of hydrogen on the benzene ring by hydroxyl renders the benzenoid ring liable to disruption at such position under alkaline permanganate attack. The presence of hydroxyl groups in the original organic matter of these horizons has been established earlier (6). If these hydroxyl groups were substituents on the benzene ring then benzene carboxylic acids would not be expected in the oxidation products.

A different experimental approach may be required to make further progress with this problem.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the technical assistance of J. G. Desjardins and R. Levick. The soil samples were supplied by G. B. Whiteside.

REFERENCES

1. Bone, W. A., L. Horton, and S. G. Ward. Researches on the chemistry of coal. IV. Its benzenoid constitution as shown by its oxidation with alkaline permanganate. *Proc. Roy. Soc., A*, 127:480-510. 1930.
2. Bone, W. A., L. G. B. Parsons, R. H. Sapiro, and C. M. Grocock. Researches on the chemistry of coal. VIII. The development of benzenoid constitution in the lignin-peat-coal-series. *Proc. Roy. Soc., A*, 148:492-522. 1934.
3. Bremner, J. M. Use of the Van Slyke-Neil manometric determination of organic and inorganic carbon in soil and organic carbon in soil extracts. *Analyst* 74:492-498. 1949.
4. Piret, E. L., R. F. Hein, E. D. Besser, and R. G. White. Oxidation of peat to organic acids. *Ind. Eng. Chem.* 49:737-741. 1957.
5. Schnitzer, M., and J. R. Wright. Extraction of organic matter from podzolic soils by means of dilute inorganic acids. *Can. J. Soil Sci.* 37:89-95. 1957.
6. Schnitzer, M., D. A. Shearer, and J. R. Wright. A study in the infrared of high-molecular weight organic matter extracted by various reagents from a podzolic B horizon. *Soil Sci.* (*In press*).
7. Van Slyke, D. D., and J. Folch. Manometric carbon determination. *J. Biol. Chem.* 136:509-541. 1940.

THE AVAILABILITY TO ALFALFA OF PHOSPHORUS FROM TWELVE DIFFERENT CARRIERS¹

J. D. BEATON² AND K. F. NIELSEN³

Canada Department of Agriculture

[Received for publication November 21, 1958]

ABSTRACT

Availabilities of the phosphorus in twelve different phosphate sources to alfalfa were determined in a growth chamber. Two crops of alfalfa were grown on two soils of high base status, Machete stony sandy loam and Westwold loam. Fertilizer materials containing monocalcium phosphate or materials such as calcium metaphosphate which are converted to monocalcium phosphate brought about the greatest increases in yield. However, yield increases also resulted from treatments with the ammonium phosphates and orthophosphoric acid. Ammonium phosphate fertilizers were the most effective in increasing the percentage of phosphorus present in the alfalfa tissue. Ammonium phosphate and monocalcium phosphate materials were equally effective in increasing total phosphorus uptake by alfalfa. The amount of CO₂ soluble phosphorus extracted from the Westwold loam, following treatment with the various phosphate sources, was correlated with the yield of the first crop of alfalfa. The average per cent P in the alfalfa tissue was found to be correlated with the CO₂ soluble P. Both the NaHCO₃ and CO₂ extractable soil phosphorus levels of the Westwold loam, after it had been treated with the different phosphate materials, were found to be highly correlated with the phosphorus uptake by the second crop of alfalfa and with the total phosphorus uptake.

INTRODUCTION

Phosphate fertilizers are frequently used to increase the yields of alfalfa grown on interior British Columbia soils. It has been pointed out by Beaton (1) that the effectiveness of the different sources, on alfalfa being grown on soils of high base status in British Columbia, varied considerably. In this study an attempt was made to evaluate the availability of phosphorus in a number of carriers to alfalfa being grown on two soils of high base status.

A number of workers have investigated the efficiency of phosphate fertilizers on several crops. Mitchell (8, 9) reported that monoammonium phosphate was superior to mono- and dicalcium phosphate in the utilization of phosphorus by grain crops grown in Saskatchewan. Similarly, Dion *et al.* (4) found that the relative efficiency of monoammonium, monocalcium and tricalcium phosphate, as phosphate sources for wheat, decreased in that order. It was shown by Owens *et al.* (13) that the phosphorus content of sugar beet plants fertilized with a high water soluble phosphate was significantly higher than for plants fertilized with a low water soluble phosphate. No differences were found, however, in the final yields of beets. In a comparison of calcium metaphosphate with concentrated superphosphate Terman and Seatz (17) found that calcium metaphosphate was, in general, a satisfactory source of phosphorus for alfalfa and other hay crops grown on calcareous soils while it was poorer than concentrated

¹ Contribution from the Field Husbandry Divisions of the Range Experimental Farm, Kamloops, B.C., and the Central Experimental Farm, Ottawa, Ont.

² Formerly Soil Specialist, Range Experimental Farm, Kamloops, B.C.; present address, Department of Soil Science, University of British Columbia, Vancouver, B.C.

³ Head, Soil Fertility Unit, Central Experimental Farm, Ottawa, Ont.

superphosphate for potatoes, sugar-beets and spring-sown small grain. The best source of phosphorus for ryegrass and Sudangrass on calcareous soils was observed by Terman *et al.* (19) to be monocalcium phosphate. Terman *et al.* (18) reported that early growth response, as determined in the greenhouse with oats and Sudangrass, and in the field with wheat forage and other crops, increased with smaller granule sizes of the low water-soluble fertilizers but decreased with smaller granule sizes of the high water-soluble fertilizers.

MATERIALS AND METHODS

Surface samples (0 to 6 inches) of two soils high in base status, the Machete stony sandy loam and the Westwold loam, were air-dried and sieved through a 10-mesh sieve. Some characteristics of the two soils are listed in Table 1.

Ten pounds of soil were placed in one-gallon glazed porcelain crocks. To reduce the influence of granule size, all the phosphate sources, with the exception of H_3PO_4 , were ground to pass a 100-mesh sieve. These materials were thoroughly mixed with each aliquot of soil before the soil was added to the crocks. One level of phosphate, 120 pounds of P_2O_5 per 2 million pounds of soil, was provided by the materials listed in Table 2. The phosphorus content of the commercial fertilizers and hydroxyapatite was determined by the method of Shelton and Harper (16). The hydroxyapatite was prepared in the laboratory according to the procedure outlined by Egan *et al.* (6). Since several of the phosphate fertilizers contained nitrogen, ammonium nitrate in solution was added to the pots to establish a uniform rate of 96 pounds of N per 2 million pounds of soil for each treatment. The treatments were replicated four times and were randomized for each soil.

Tensiometers were used to indicate soil moisture tension in the crocks. Immediately following the installation of the tensiometers the soil was moistened and maintained at approximately 0.2 atm. for a period of 3 weeks. After this period, as well as at the end of the experiment, small samples of soil were taken from each crock. Total phosphorus, carbonic acid and $NaHCO_3$ extractable phosphorus were determined on these samples. Ten germinated Grimm alfalfa seeds, which had been inoculated, were then placed in each crock. The plants were later thinned to leave a total of five. When the soil moisture tension reached 0.8 atm., sufficient water was added to lower it to 0.2 atm.

The crocks were placed in a growth chamber at Kamloops, where the radiant energy was supplied by a light assembly consisting of cool white fluorescent tubes and red incandescent bulbs. To provide a light intensity of 1000 foot candles at the top of the alfalfa plants, the light assembly was maintained at a height of about 8 inches above the plants. Alternating periods of 16 hours of light and 8 hours of darkness were maintained throughout the duration of the experiment. While the lights were on, the temperature remained at about 80° F.; when they were off it was about 60° F. Two crops of alfalfa were harvested, the first 6 weeks following planting, and the second approximately 4 weeks after the first harvest.

The tissue was then dried at 70° C., weighed, ground in a Wiley Mill and stored for analysis.

TABLE 1.—SOME PROPERTIES OF SURFACE SOIL (0-6 INCHES) OF THE MACHETE STONY SANDY LOAM AND THE WESTWOLD LOAM

Soil	Cation exch. cap., me. per 100 gm. of soil	Exchangeable cations me. per 100 gm. of soil				pH of soil paste	Conductivity mmhos.	Organic matter per cent	Total P p.p.m.	Extractable P p.p.m.		Content of sand, silt and clay fines per cent
		Ca ⁺⁺	Mg ⁺⁺	K ⁺	Na ⁺					H ₂ CO ₃	NaHCO ₃	
Machete stony sandy loam	21.41	17.55	3.43	0.38	0.05	7.68	1.90	4.4	855	14	30	57.7 22.4 19.9
Westwold loam	35.50	21.09	11.43	2.67	0.31	7.60	2.94	4.3	971	8	40	42.9 36.0 21.1

TABLE 2.—ANALYSES OF PHOSPHATE CARRIERS USED IN THE EXPERIMENT

Formula	Common name	N per cent	P ₂ O ₅ per cent	CaO per cent	P ₂ O ₅ /CaO (weight ratio)	SO ₄ ²⁻ per cent
11-48-0	Ammonium phosphate ¹	11.4	48.8	1.9	25.68	8.7
16-20-0	Ammonium phosphate sulphate ¹	16.7	20.4	1.6	12.75	45.8
0-19-0	Ordinary superphosphate ²	—	20.2	10.2	1.98	36.4
0-45-0	Concentrated superphosphate ²	—	45.4	20.3	2.23	3.5
0-62-0	Calcium metaphosphate	—	63.1	27.1	2.32	—
H ₃ PO ₄	Orthophosphoric acid	—	72.4	—	—	—
Ca(H ₂ PO ₄) ₂ ·H ₂ O	Monocalcium phosphate (monohydrate)	—	56.3	22.3	2.52	—
CaHPO ₄ ·2H ₂ O	Dicalcium phosphate (dihydrate)	—	41.2	32.6	1.26	—
Ca ₃ (PO ₄) ₂	Tricalcium phosphate	—	45.8	54.2	0.85	—
Ca ₁₀ (PO ₄) ₆ (OH) ₂	Hydroxyapatite	—	42.4	55.8	0.76	—
NH ₄ H ₂ PO ₄	Mon ammonium phosphate	12.2	61.7	—	—	—
(NH ₄) ₂ HPO ₄	Diammonium phosphate	21.2	53.8	—	—	—

¹ Active phosphate compound is monoammonium phosphate.² Active phosphate compound is monocalcium phosphate.

Cation exchange capacity, exchangeable cations and conductivity of the soil-saturation extract were determined according to the methods outlined by the U. S. Salinity Laboratory (21). Soil pH was determined on the soil paste as advocated by Doughty (5). The organic matter determinations were made by the method described by Peech *et al.* (14). Total phosphorus in the soil and plant samples was determined by the procedure of Shelton and Harper (16). The carbonic acid extraction of soil phosphorus was a modification of the CO_2 extraction procedure used by Wilcox* and the technique advocated by the National Soil and Fertilizer Research Committee (10). The NaHCO_3 extractable phosphorus was determined by the procedure of Olsen *et al.* (12). Percentages of sand, silt and clay were determined by the Bouyoucos hydrometer method (2).

RESULTS AND DISCUSSION

Yields of alfalfa forage are summarized in Table 3. In the case of the first cut, treatment with 11-48-0, 16-20-0, 0-19-0, 0-45-0, 0-62-0 and H_3PO_4 on the Machete stony sandy loam all gave yields significantly larger than that of the no phosphorous treatment. The 0-62-0 treatment gave a significantly higher yield than any of the other phosphate sources. With the exception of the 0-62-0 treatment, 0-45-0 gave a significantly greater yield than the other phosphorus supplements. The response of alfalfa to 0-62-0 in the first cut is somewhat surprising since the data of Hignett** indicated that calcium metaphosphate dissolved slowly in water with the formation of soluble nonorthophosphates which gradually hydrolyzed to orthophosphates. Tisdale and Nelson (20) stated that calcium meta-

* Personal communication (per Stevenson, D.S.), 1953.

** Hignett, T. P., Chief, Development Branch, Div. Chem. Development, Tennessee Valley Authority. Personal communication, 1957.

TABLE 3.—YIELDS OF ALFALFA FROM TWO SOILS TREATED WITH SEVERAL PHOSPHATE CARRIERS

Source of phosphorus	Yields per pot-gm. oven dry material					
	Machete stony sandy loam			Westwold loam		
	1st cut	2nd cut	Total	1st cut	2nd cut	Total
11-48-0	3.95	1.34	5.29	2.08	3.37	5.45
16-20-0	4.17	1.83	6.00	2.62	2.98	5.60
0-19-0	4.07	1.59	5.66	2.85	3.69	6.54
0-45-0	4.55	1.99	6.54	2.40	3.69	6.09
0-62-0	4.98	1.88	6.86	2.35	3.59	5.94
H_3PO_4	4.09	1.64	5.73	2.04	3.12	5.16
$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	3.11	1.74	4.85	2.51	3.34	5.85
$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	3.44	1.74	5.18	1.89	2.65	4.54
$\text{Ca}_3(\text{PO}_4)_2$	3.37	1.37	4.74	1.96	2.50	4.46
$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	2.92	1.39	4.31	2.00	2.78	4.78
$\text{NH}_4\text{H}_2\text{PO}_4$	3.44	1.56	5.00	2.28	3.47	5.75
$(\text{NH}_4)_2\text{HPO}_4$	3.29	1.88	5.17	2.58	2.85	5.43
No P	3.34	1.27	4.61	1.63	2.83	4.46
L.S.D.	0.32 (5%) 0.45 (1%)	0.28 (5%) 0.40 (1%)	0.93 (5%) 1.31 (1%)	0.37 (5%) 0.52 (1%)	0.67 (5%) 0.94 (1%)	0.79 (5%) 1.36 (1%)

phosphate generally reacts too slowly in alkaline soils to show much response in the first year. They indicated, however, that more favourable results have been obtained with it on calcareous soils than with di- or tricalcium phosphates. Newman and Hill (11) concluded that, although calcium metaphosphate is classed by conventional fertilizer criteria as a water-insoluble phosphate, the quality of its insolubility is different from that of the common insoluble phosphates because it can absorb water slowly and change to soluble monocalcium phosphate.

Significant increases in yield above that of the check were obtained in the second harvest by the treatments with 16-20-0, 0-19-0, 0-45-0, 0-62-0, H_3PO_4 , $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$. Concentrated superphosphate gave significantly higher results than all the above treatments with the exception of 0-62-0 and $(\text{NH}_4)_2\text{HPO}_4$. Both 0-62-0 and $(\text{NH}_4)_2\text{HPO}_4$ gave significantly higher yields than 0-19-0 and $\text{NH}_4\text{H}_2\text{PO}_4$. Applications of $\text{Ca}_3(\text{PO}_4)_2$, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and 11-48-0 did not bring about increases in yield. The observation that 0-62-0 and 0-45-0 treatments resulted in comparable yields of alfalfa is in accordance with the findings of Terman and Seatz (17) as well as other earlier workers. The total yield was found to be significantly increased by the addition of 16-20-0, 0-19-0, 0-45-0, 0-62-0 and H_3PO_4 . Of these treatments only 0-62-0 was significantly greater than H_3PO_4 .

With respect to the Westwold loam, 11-48-0, 16-20-0, 0-19-0, 0-45-0, 0-62-0, H_3PO_4 , $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ all gave significant increases in the yield of the first cut. The 0-19-0 source gave the highest yield and significantly outyielded 11-48-0, 0-45-0, 0-62-0, H_3PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$. It was also found that 16-20-0 caused significantly larger yields than 11-48-0 and H_3PO_4 . Once again $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ did not appreciably affect the yields of alfalfa. There is some evidence of a response to sulphur as well as phosphorus on the Westwold loam. Both 0-19-0 and 16-20-0, which contained 36.4 and 45.8 per cent SO_4 , respectively, brought about larger increases in yield than their respective counterparts, 0-45-0 and 11-48-0 which contained considerably less sulphur. This sulphur response appears to have occurred only in the early stages of plant growth since a similar response was not observed in the second harvest. Only 0-19-0, 0-45-0 and 0-62-0 treatments resulted in increased yields of the second harvest of alfalfa from the Westwold loam. The total yield of the 11-48-0, 16-20-0, 0-19-0, 0-45-0, 0-62-0, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, and $(\text{NH}_4)_2\text{HPO}_4$ treatments was found to be significantly greater than that of the check. Of these treatments, 11-48-0, 16-20-0 and $(\text{NH}_4)_2\text{HPO}_4$ gave total yields that were less than that of the 0-19-0 treatment.

It is evident that for both soils and for both harvests the monocalcium phosphate form and materials, such as calcium metaphosphate, which are gradually converted to monocalcium phosphate, were more effective than the dicalcium phosphate form. On the Machete stony sandy loam however, the $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ treatment was generally not effective, even though other materials such as 0-19-0 and 0-45-0, which contain this form

of phosphate, were effective. There appears to be no satisfactory explanation for this discrepancy. Lehr and Brown (7) suggested that the superiority of monocalcium phosphate over dicalcium phosphate dihydrate was related to the greater specific surface and wider distribution of the phosphate formed from monocalcium phosphate. The greater response to monocalcium phosphate was also believed to be related to phosphate made available during hydrolysis of dicalcium phosphate dihydrate to octaphosphate, which was found to be greater in the monocalcium phosphate treatment. The hydrolytic reactions were pictured as follows:



The hydrolysis of dicalcium phosphate dihydrate, which is formed by hydrolysis from monocalcium phosphate, was believed to enhance the availability of part of the phosphorus to the plant in either of two ways:

1. $4 \text{CaHPO}_4 \cdot 2\text{H}_2\text{O} \longrightarrow \text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O} + \text{H}_2\text{PO}_4 + 5\text{H}_2\text{O}$. (H_2PO_4 may be readily available).
2. If the concentration of P in the fertilizer zone is governed by the solubility product of dicalcium phosphate, the removal of excess Ca^{++} ions by precipitation of the octocalcium phosphate would permit a higher concentration of phosphate to exist. Lehr and Brown also pointed out that in alkaline soils the presence of plants tended to bring about even greater hydrolysis of monocalcium phosphate with the formation of octaphosphate. Presumably, the plant roots absorbed phosphate leaving the excess Ca^{++} ions to be precipitated as octaphosphate or apatite.

The greater effectiveness of monocalcium phosphate over dicalcium phosphate dihydrate in such soils may also be explained by the existence of soil solutions supersaturated with respect to dicalcium phosphate. Clark and Turner (3) recognized, in a study of reactions between solid calcium carbonate and orthophosphate solutions, the presence of solutions that were supersaturated with respect to dicalcium phosphate. If such supersaturated solutions existed in soils of high base status, it is possible that growing plants could readily utilize the temporary excess of phosphate in solution.

The ammonium phosphate fertilizers also brought about increases in the yield of alfalfa from both soils. However, these increases in yield were not as large as those resulting from the monocalcium phosphate treatments. This observation is in accordance with the suggestion by Beaton (1) that the ammonium phosphate bearing fertilizers, such as 11-48-0 and 16-20-0, were not as effective as the monocalcium fertilizers for perennial crops, such as alfalfa, being grown on soils of high base status. In view of the work reported by Clark and Turner (3), where hydroxyapatite was shown to be the thermodynamically stable form of phosphate in calcareous and alkaline soils, and because its rate of formation will be dependent on the concentration of phosphate, particularly PO_4^{3-} , in solution, it was believed by Beaton that the highly soluble ammonium phosphate provided adequate phosphate for the ready precipitation of hydroxyapatite. If the formation of hydroxyapatite was favoured, the amount of phosphate in the soil solution available for plant growth would be considerably decreased, whereas the monocalcium phosphate materials would be converted to dicalcium phosphate and eventually to octaphosphate and

TABLE 4.—PER CENT PHOSPHORUS IN ALFALFA AND GRAMS OF PHOSPHORUS REMOVED FROM TWO SOILS TREATED WITH SEVERAL PHOSPHATE CARRIERS

Source of phosphorus	Phosphorus content—per cent					Phosphorus removed—gm. per pot						
	Machete stony sandy loam					Machete stony sandy loam			Westwold loam			
	1st cut	2nd cut	Average	1st cut	2nd cut	Average	1st cut	2nd cut	Total	1st cut	2nd cut	Total
11-48-0	0.338	0.370	0.354	0.324	0.321	0.323	1.34	0.50	1.84	0.67	1.08	1.75
16-20-0	0.345	0.364	0.355	0.313	0.353	0.333	1.44	0.67	2.11	0.82	1.05	1.87
0-19-0	0.337	0.332	0.335	0.308	0.330	0.319	1.37	0.53	1.90	0.88	1.22	2.10
0-45-0	0.316	0.337	0.327	0.292	0.351	0.322	1.44	0.67	2.11	0.70	1.26	1.96
0-62-0	0.316	0.335	0.326	0.235	0.347	0.291	1.58	0.63	2.21	0.67	1.25	1.92
H ₂ PO ₄	0.327	0.309	0.318	0.303	0.359	0.331	1.44	0.50	1.94	0.62	1.12	1.74
Ca(H ₂ PO ₄) ₂ ·H ₂ O	0.309	0.330	0.320	0.304	0.351	0.328	0.96	0.58	1.54	0.76	1.17	1.93
CaHPO ₄ ·2H ₂ O	0.315	0.340	0.328	0.247	0.362	0.305	1.08	0.59	1.67	0.47	0.96	1.43
Ca ₂ (PO ₄) ₂	0.292	0.317	0.305	0.264	0.315	0.290	0.99	0.43	1.42	0.52	0.79	1.31
Ca ₁₀ (PO ₄) ₆ (OH) ₂	0.287	0.304	0.296	0.254	0.341	0.298	0.84	0.42	1.26	0.51	0.95	1.46
NH ₄ H ₂ PO ₄	0.306	0.332	0.319	0.310	0.349	0.330	1.05	0.52	1.57	0.71	1.21	1.92
(NH ₄) ₂ HPO ₄	0.319	0.362	0.341	0.341	0.360	0.351	1.05	0.68	1.73	0.88	1.03	1.91
No P	0.314	0.315	0.315	0.273	0.345	0.309	1.05	0.39	1.44	0.45	0.98	1.43
L.S.D.	0.013 (5%)	0.026 (5%)	0.025 (5%)	0.040 (5%)	N.S.	N.S.	0.25 (5%)	0.12 (5%)	0.34 (5%)	0.09 (5%)	0.23 (5%)	0.26 (5%)
	0.019 (1%)	0.037 (1%)	0.035 (1%)	0.057 (1%)			0.35 (1%)	0.17 (1%)	0.47 (1%)	0.13 (1%)	0.33 (1%)	0.37 (1%)

hydroxyapatite. With such a conversion there probably would be sufficient phosphate in solution for plant growth but not enough to permit the rapid formation of hydroxyapatite.

The per cent phosphorus present in the alfalfa tissue is given in Table 4. With the Machete stony sandy loam the 11-48-0, 16-20-0, 0-19-0 and H_3PO_4 treatments resulted in significant increases in the first cut. The per cent P value with the 16-20-0 treatment was significantly larger than with the H_3PO_4 treatment. In the second cut and in the average phosphorus content only the 11-48-0, 16-20-0 and $(NH_4)_2HPO_4$ treatments brought about significant increases in the percentage of phosphorus present in the alfalfa tissue. The results obtained from the alfalfa grown on the Westwold loam were significant for the first harvest only. Three treatments, 11-48-0, 16-20-0 and $(NH_4)_2HPO_4$, were found to give significantly higher values than the check.

From the above results it appears that ammonium phosphate fertilizers were the most effective in raising the phosphorus content of alfalfa. This observation is in agreement with the results obtained by Owens *et al.* (13), where it was found that the phosphorus content of sugar beets was higher with a high water soluble fertilizer than with a low water soluble fertilizer. The increase in percent P in the alfalfa tissue may be the result of the presence of the NH_4^+ ion. Rennie and Soper (15) reported that NH_4^+ had a stimulative effect on phosphorus uptake by wheat during the early stages of growth. It was found also that placement was important, as increased phosphorus uptake occurred only when the ammonium ion was intimately associated with the fertilizer phosphorus.

This stimulative effect may partially explain the response of alfalfa to the ammonium phosphate fertilizers. If the NH_4^+ ion does enhance phosphorus uptake and if optimum levels of NH_4^+ ion do not exist, diammonium phosphate may prove to be more effective than monoammonium phosphate since it has more ammonium per unit concentration of phosphate.

The high phosphorus content of alfalfa that resulted from treatment with the ammonium phosphate fertilizer materials may also have been due to the initial high water solubility of these materials which would have permitted rapid absorption by plants. Later, upon conversion of the soluble phosphate to hydroxyapatite, as postulated previously, a reduction in plant uptake and plant growth would probably occur. Any subsequent growth with less phosphorus being absorbed would thus tend to dilute the initial high phosphorus content to the values observed.

The results of phosphorus uptake, which are also recorded in Table 4, show that the additions of 11-48-0, 16-20-0, 0-19-0, 0-45-0, 0-62-0 and H_3PO_4 were responsible for significant increases over the check with the first crop and with the total phosphorus uptake by alfalfa grown on the Machete stony sandy loam. The 0-62-0 treatment was found to result in significantly more total phosphorus uptake than the 11-48-0 and H_3PO_4 treatments. Significant increases in the phosphorus uptake by the second cut were obtained with 16-20-0, 0-19-0, 0-45-0, 0-62-0, $Ca(H_2PO_4)_2 \cdot H_2O$, $CaHPO_4 \cdot 2H_2O$, $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$. The phosphorus uptake in the first harvest of alfalfa and the total P uptake from the Westwold loam

was increased significantly by the 11-48-0, 16-20-0, 0-19-0, 0-45-0, 0-62-0, H_3PO_4 , $Ca(H_2PO_4)_2 \cdot H_2O$, $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$ treatments. In the first harvest the values for 16-20-0, 0-19-0, and $(NH_4)_2HPO_4$ were significantly greater than for the rest. Significantly more total phosphorus uptake occurred with the 0-19-0 treatment than with the 11-48-0 and H_3PO_4 treatments. Phosphorus uptake by the second harvest of alfalfa from the Westwold loam was significantly increased by 0-19-0, 0-45-0, 0-62-0 and $NH_4H_2PO_4$.

The correlation coefficients (r) were calculated relating $NaHCO_3$ and H_2CO_3 extractable soil phosphorus to yield, per cent phosphorus in tissue and phosphorus uptake by alfalfa grown on the Westwold loam. There was no correlation between $NaHCO_3$ extraction and yield. The CO_2 extraction was correlated ($r = 0.58$) with yields in the first cut but not with second cut. The average per cent P was found to be correlated ($r = 0.56$) with only CO_2 soluble P. Both the $NaHCO_3$ ($r = 0.89$ and 0.81) and CO_2 ($r = 0.93$ and $r = 0.60$) extractable soil phosphorus values were found to be highly correlated with phosphorus uptake by the second crop and with the total phosphorus uptake. Terman *et al.* (19) reported a significant correlation between the phosphorus extracted by 0.5 N $NaHCO_3$ and the phosphorus uptake by ryegrass and Sudangrass from six different phosphate sources.

REFERENCES

1. Beaton, J. D. Fertility problems encountered in forage crop production on B. C. Interior soils under irrigation and dryland farming. Report, B. C. Agronomists' Conference. 1957.
2. Bouyoucos, G. J. A recalibration of the hydrometer method for making mechanical analysis of soil. *Amer. Soc. Agron. J.* 43:434-437. 1951.
3. Clark, J. S., and R. C. Turner. Reactions between solid calcium carbonate and orthophosphate solutions. *Can. J. Chem.* 33:665-671. 1955.
4. Dion, H. G., J. W. T. Spinks, and J. Mitchell. Experiments with radiophosphorus on the uptake of phosphorus by wheat. *Sci. Agr.* 29:512-526. 1949.
5. Doughty, J. L. The advantage of a soil paste for routine pH determinations. *Sci. Agr.* 22:135-138. 1941.
6. Egan, Edward P., Jr., Zachary T. Wakefield, and Kelly L. Elmore. High temperature heat content of hydroxyapatite. *J. Amer. Chem. Soc.* 72:2418-2421. 1950.
7. Lehr, J. R., and W. E. Brown. Calcium phosphate fertilizers. II. A petrographic study of their alteration in soils. *Soil Sci. Soc. Amer. Proc.* 22:29-32. 1958.
8. Mitchell, J. The effects of phosphate fertilizers on summer fallow wheat crops in certain areas of Saskatchewan. *Sci. Agr.* 26:566-577. 1946.
9. Mitchell, J. A review of tracer studies in Saskatchewan on the utilization of phosphates by grain crops. *J. Soil Sci.* 8:73-85. 1957.
10. National Soil and Fertilizer Research Committee. Soil testing in the United States. 1951.
11. Newman, E. L., and W. L. Hill. New and better fertilizers. *U.S.D.A. Yearbook of Agriculture*, pp. 210-216. Washington, D. C. 1957.
12. Olsen, S. R., C. V. Cole, F. Watanabe, and L. A. Dean. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. *U.S.D.A. Circ.* 939. Washington, D. C. 1954.
13. Owens, L., K. Lawton, L. S. Robertson, and C. Apostolakis. Laboratory, greenhouse and field studies with mixed fertilizers varying in water-soluble phosphorus content and particle size. *Soil Sci. Soc. Amer. Proc.* 19:315-319. 1955.
14. Peech, M., L. T. Alexander, L. A. Dean, and J. F. Reed. Methods of soil analysis for soil fertility investigations. *U.S.D.A. Circ.* 757. Washington, D. C. 1947.

15. Rennie, D. A., and R. J. Soper. The effect of nitrogen additions on fertilizer-phosphorus availability. II. *J. Soil Sci.* 9:155-167. 1958.
16. Shelton, W. R., and H. J. Harper. A rapid method for the determination of total phosphorus in soil and plant material. *Iowa State Coll. J. Sci.* 15:403-413. 1941.
17. Terman, G. L., and L. F. Seatz. Crop response to metaphosphate fertilizers. *Soil Sci. Soc. Amer. Proc.* 20:375-378. 1956.
18. Terman, G. L., J. L. Anthony, W. P. Mortensen, and J. A. Lutz, Jr. Crop response to NPK fertilizers varying in granule size and water solubility of phosphorus. *Soil Sci. Soc. Amer. Proc.* 20:551-556. 1956.
19. Terman, G. L., D. R. Bouldin, and J. R. Lehr. Calcium phosphate fertilizers. I. Availability to plants and solubility in soils varying in pH. *Soil Sci. Soc. Amer. Proc.* 22:25-29. 1958.
20. Tisdale, Samuel L., and L. Nelson Werner. *Soil fertility and fertilizers.* MacMillan Co., New York, N. Y. 1956.
21. U. S. Salinity Laboratory Staff. *Diagnosis and improvement of saline and alkali soils.* U. S. D. A. Handbook 60. Washington, D.C. 1954.

ADSORPTION OF PHOSPHORUS BY FOUR SASKATCHEWAN SOILS¹

D. A. RENNIE AND R. B. MCKERCHER²

University of Saskatchewan, Saskatoon, Saskatchewan

[Received for publication August 25, 1958]

ABSTRACT

The adsorption of phosphorus by four soils of differing colloid content showed close agreement with the Langmuir isotherm when final phosphorus solution concentrations were less than 20 $\mu\text{g. P/ml.}$ Calculated adsorption maximum for the four soils were 79.1, 87.7, 150.4 and 164.4 $\mu\text{g. P per g. of soil.}$ The average value of the constant k , related to the bounding energy of the soil for phosphorus, was 0.141.

The percentage phosphorus saturation of the adsorption maximum was closely correlated with the equilibrium phosphorus concentration in the soil suspension. At an equilibrium concentration of 28.7 $\mu\text{g. P/ml.}$, 100 per cent saturation of the adsorption capacity of the four soils was obtained; the total adsorbed phosphorus on the four soils was not related to the phosphorus concentration of the soil solution but varied considerably depending on the colloid content of the respective soils.

Carbonated water extractable phosphorus, and 'surface' phosphorus measured by P32 equilibrium studies, were not related to the equilibrium concentration of phosphorus of the soil solution. It appears that the percentage phosphorus saturation of the adsorption maximum may prove a more reliable measure of the capacity of the soil to supply phosphorus to the soil solution than either of the 'quick' tests used.

Organic matter appeared to be equally as important as the inorganic colloids in determining the phosphorus adsorption capacity of the soils. Differences in exchangeable calcium were not closely related to the adsorption maximum.

Three extractants, carbonated water, sodium bicarbonate and ion exchange resins, are at present being used to predict the phosphorus-supplying power of Saskatchewan soils. These extractants have been used with varying degrees of success but, in general, have not given data which correlate with yield responses from phosphorus fertilization. Recent studies (5, 13) have suggested that adsorbed soil phosphorus may possibly include, or have an important influence on, plant available phosphorus.

This study was undertaken to investigate adsorption of phosphorus by soils of differing clay and organic matter content, and to relate this adsorbed phosphorus to "available" (H_2CO_3 extractable) phosphorus.

An adsorption isotherm may be defined (14) as the relation between the amount of a substance adsorbed by an adsorbant and the equilibrium concentration of the substance at constant temperature. Phosphorus adsorption data on soils have commonly been described by the Freundlich isotherm (1, 4, 8, 15). This empirical equation is not specific, in that it applies to a wide range of equilibrium phosphorus concentrations. In contrast, the Langmuir isotherm has a sound theoretical derivation, is specific for smaller amounts of adsorbed phosphorus and more dilute equilibrium phosphorus concentrations (more likely to be encountered in normal fertilizer applications of phosphorus), and an adsorption maximum

¹ Contribution from the Department of Soil Science, University of Saskatchewan, Saskatoon. Presented at 3rd Annual Convention, Canadian Society of Soil Science, Vancouver, B. C., June 24-28, 1957.

² Associate Professor of Soil Science, and Soil Specialist, respectively.

can be calculated. Olsen and Watanabe (13), and Fried and Shapiro (5) have shown that constants calculated from the Langmuir isotherm permit a sound theoretical approach to some of the problems of phosphorus retention in soils.

The Langmuir adsorption equation (9) may be written in the form: $x/m = \frac{kbc}{1+kc}$. In linear form this equation becomes $\frac{c}{x/m} = \frac{1}{kb} + \frac{c}{b}$ where c = the final solution concentration (equilibrium concentration) in $\mu\text{g. P/ml}$, $\frac{x}{m} = \mu\text{g. P adsorbed per g. of soil}$, b = the adsorption maximum and k = a constant related to the bonding energy of the soil colloids for the phosphorus. A straight line plot of $\frac{c}{x/m}$ against c can be assumed to be indicative of an adsorption reaction. In such a case, the adsorption maximum and the energy of adsorption can readily be calculated, and it can be assumed that the conditions are such that a unimolecular adsorbed layer is present on the surface of the colloids.

EXPERIMENTAL

Adsorption Studies

Typical time adsorption curves indicate an initial fast reaction followed by a secondary reaction which proceeds at a slow and almost constant rate (8, 17, 20). While most workers studying phosphorus adsorption have

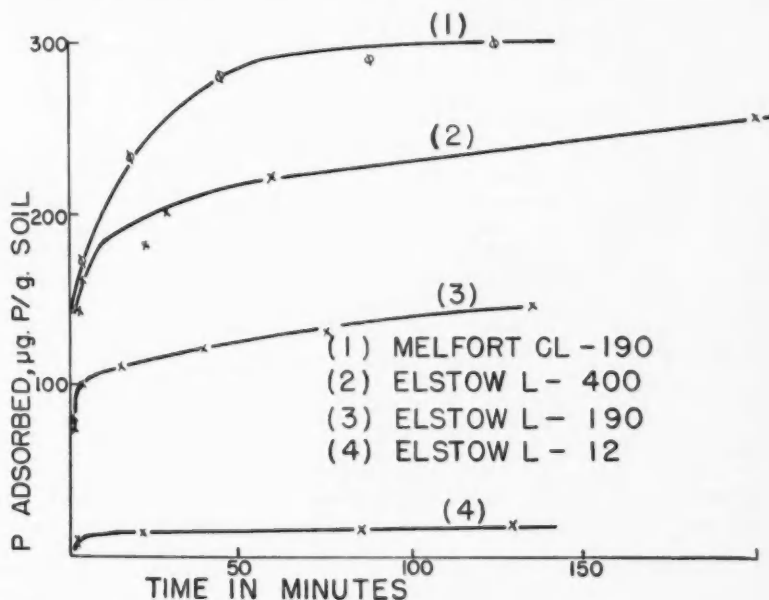


FIGURE 1. Time adsorption curves obtained on Melfort and Elstow soil.

attempted to adjust the time of contact to where the rate of change of the amount of phosphorus in solution is small, contact periods have ranged from a few minutes to a week or more. For example, Kurtz *et al.* (8) allowed 24 hours for equilibrium to become established between the soil and solution while Seatz (17) used a 4-day contact period.

One hundred ml. of KH_2PO_4 solutions containing 12, 190 and 400 p.p.m. of P per ml. were shaken with 10-g. soil samples for periods of contact ranging from 1 minute to 72 hours. A portion of the data obtained is given in Figure 1. Both soil type and initial phosphorus concentration altered the rate of the initial or 'adsorption' reaction and the second or 'fixation' phenomenon. The data indicate that a 1-hour shaking time would permit completion of the adsorption reaction and eliminate complicating secondary reactions. However, in subsequent adsorption studies, it was found that a 6-hour shaking time was preferable, due to the difficulty in obtaining agreement between duplicates at shorter periods of contact.

Data for plotting the Langmuir isotherm were obtained using a similar procedure to that described by Cole *et al.* (3). Ten g. of air dry soil, ground to pass a 1-mm. screen, were shaken in 100 ml. of KH_2PO_4 solutions of varying concentrations. The pH of the phosphorus solutions were adjusted to 7. (Soil to solution ratios of 1:200, 1:100 and 1:10 were used, but only the latter ratio gave reproducible adsorption curves). The suspensions were shaken for 6 hours on an end-over-end shaker, filtered, and the phosphorus concentrations of the filtrate determined to obtain the amount of phosphorus adsorbed by the soil. Analysis for phosphorus was made by the Truog and Meyer method (19) as modified by St. Arnaud (16), where the phosphorus content of the solution was less than 1 p.p.m. and by the hydrazene sulphate method proposed by Shelton and Harper (19) for more concentrated solutions.

Surface-phosphorus Measurements

Surface phosphorus was measured on separate soil samples, using a procedure similar to that of McAuliffe (10). A 50-g. soil sample was shaken in 50 ml. water for 24 hours. One ml. of a solution containing 2 μC . of carrier-free P32 was added and the shaking continued for an additional hour. The suspension was then centrifuged and aliquots of the supernatant removed for P31 and P32 analysis. The activity measurements were carried out using a D.M. 6 thin-walled Beta Geiger tube* with a removable glass container for the liquid. The amount of 'surface' phosphorus was calculated from the isotope dilution law at isotopic equilibrium—

$$\text{P31 (surface)} = \frac{\text{P32 (surface)}}{\text{P32 (solution)}} \times \text{P31 (solution)}$$

CO₂ Extraction Studies

The relationship between adsorbed and extractable phosphorus was determined as follows: The soil suspensions from the adsorption studies were centrifuged, the liquid decanted, and the soil washed into evaporating dishes. The soils were air dried and the CO₂ extractable phosphorus determined following the procedure of McGeorge (11) as modified by St. Arnaud (16).

* 20th Century Electronics Ltd., New Addington, Croydon, Surrey, England.

TABLE 1.—CHARACTERISTICS OF SOILS USED

Soil type	Description	Mechanical analyses percentage			Loss ¹	pH	%N	Exchangeable bases me/100 g. soil			
		Sand	Silt	Clay				Ca++	Mg++	K+	Na+
Elstow Loam	Dark brown soil developed on medium textured lacustrine deposits	33.4	44.4	16.8	5.4	6.5	.171	6.1	4.9	2.4	0.7
Weyburn Loam	Dark brown soil developed on glacial till deposits	37.8	35.9	20.5	5.8	7.0	.244	15.8	5.2	2.3	0.2
Oxbow Loam	Shallow black soil developed on glacial till deposits	30.5	40.4	20.5	8.6	7.2	.354	19.2	6.5	1.9	0.1
Melfort SICL	Deep black soil developed on heavy-textured lacustrine deposits	16.5	36.7	35.0	11.8	6.5	.416	31.2	8.7	1.8	0.1

¹ Non-recoverable material after HCl and H₂O₂ treatment

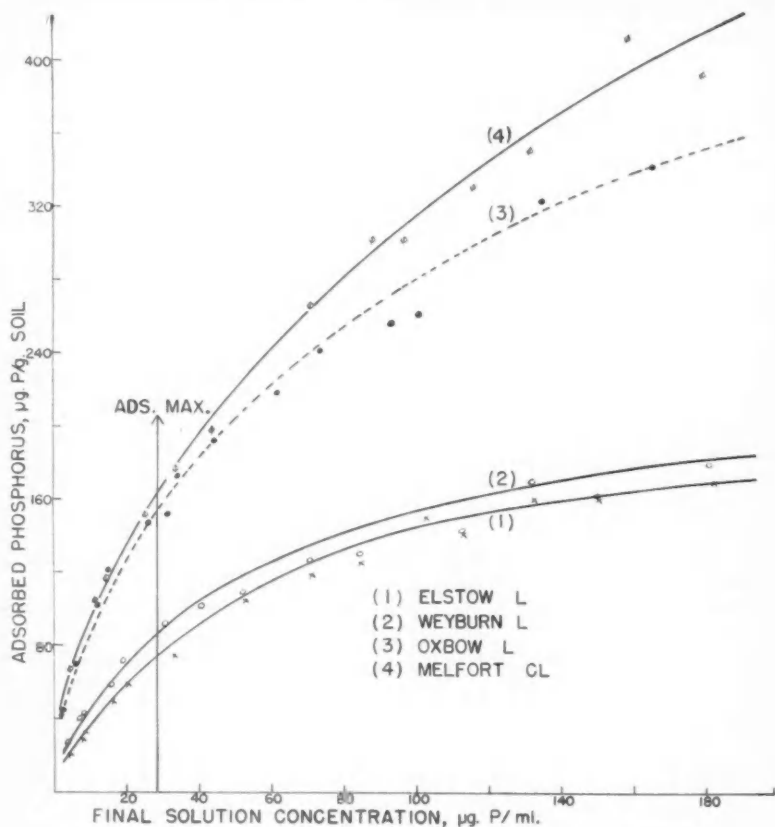


FIGURE 2. Phosphorus adsorption isotherms for the Melfort, Oxbow, Weyburn and Elstow soils.

Soil Samples

Four surface soils of differing clay and organic matter content were used. Specific information on the soils is given in Table 1. The mechanical analysis was done by the standard pipette procedure, total nitrogen by the micro-Kjeldahl method, pH was determined on the saturated paste, and extractable phosphorus by CO_2 extraction. Exchangeable bases were run on ammonium acetate extractions using the flame spectrophotometer. These methods are outlined in the Saskatchewan Soil Survey Manual*.

RESULTS

Surface-phosphorus

Since it was not feasible to obtain soils free of adsorbed phosphorus, the amount of surface phosphorus on the four soils was determined. The data are given in Table 2. The amount of phosphorus present as surface

* St. Arnaud, R. J. Manual of laboratory methods. Dept. of Soil Science, Univ. of Sask., Saskatoon. 1956.

TABLE 2.—SURFACE PHOSPHORUS AND ADSORPTION OF P32

Soil type	Surface P $\mu\text{g./g. soil}$	% P32 adsorbed on the soil
Elstow	10.13	51
Weyburn	10.32	68
Oxbow	10.93	83
Melfort	11.37	85

phosphorus did not differ appreciably for the four soils. The per cent of added P32 that was adsorbed on the soils varied considerably, being least for the Elstow, intermediate for the Weyburn and very high for the Oxbow and Melfort soils. This suggests that the adsorbing capacity of the Black soils is similar and much higher than the two Dark Brown soils.

Adsorbed Phosphorus

Phosphorus adsorption isotherms obtained for the Elstow, Weyburn, Oxbow and Melfort soils are illustrated in Figure 2. All data have been corrected for the amount of surface-phosphorus present initially on the soils. While each soil exhibited different adsorption characteristics, the curves obtained from the phosphorus adsorption data are similar to the Type 1 adsorption curve given by Prutton and Maron (14). The relative adsorption of phosphorus by the soils at low final solution concentrations is similar to that obtained with the P32 equilibrium studies (Table 2); the soils can be arranged in the following order of increasing adsorption of phosphorus—Elstow, Weyburn, Oxbow and Melfort. (At low concentrations the adsorption by the latter two soils was practically identical). The flexpoint of the four adsorption isotherms occurred at 50-60 $\mu\text{g. P/ml}$. Beyond this point, the curves approached a straight line, continuing upward to the highest concentration used—800 $\mu\text{g. P/ml}$.

The adsorption data, plotted according to the Langmuir equation, are illustrated in Figure 3. The data show satisfactory agreement with the Langmuir isotherm as a straight line relationship was obtained for the four soils. The isotherms for all soils break in the vicinity of a final solution concentration of 20 $\mu\text{g. P per ml}$. This is in agreement with Olsen (13), who also reported that adsorption data did not conform with the Langmuir isotherm where final solution concentrations greater than 18-20 $\mu\text{g/ml}$. were used.

Calculated adsorption maximum for the soils are given in Figure 3. These maxima all fall on a line parallel to the y axis (see Figure 2); this line cuts the x axis at a final solution concentration of 28.7 $\mu\text{g/ml}$. This suggests that a close relationship may exist between percentage saturation of the adsorption maximum and final solution concentration. The relationship between these two variables for the four soils is illustrated in Figure 4. The highly significant correlation of 0.935 between the percentage saturation of the adsorption maximum and the corresponding final solution concentration for the four soils indicates that the equilibrium

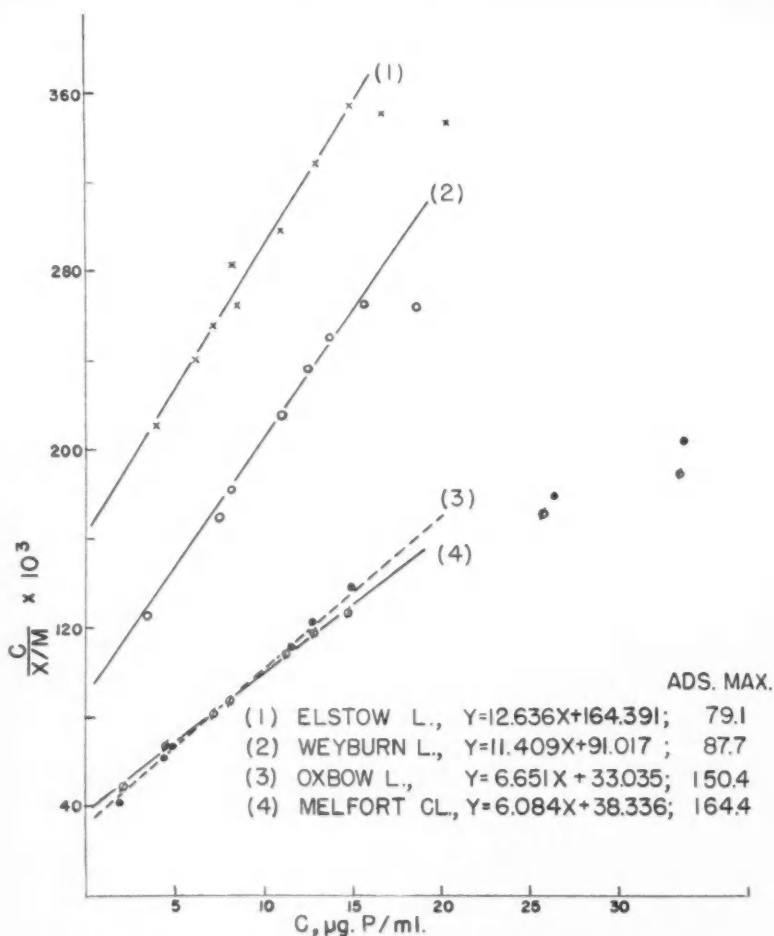


FIGURE 3. Langmuir plot of adsorption data for the Elstow, Weyburn, Oxbow, and Melfort soils.

concentrations of phosphorus in a soil suspension closely reflects the degree of phosphorus saturation on the adsorbing surfaces of the soil colloids. This relationship breaks at 100 per cent saturation, and the slope of the line changes. If no further adsorption had occurred, the line would have risen parallel to the y axis. Either new centres of adsorption have been formed (possibly precipitated phosphates) or multi-molecular layers of adsorbed phosphorus occurred. This latter phenomena has been shown to occur with gas adsorption where pressures approaching the saturation value are used (6).

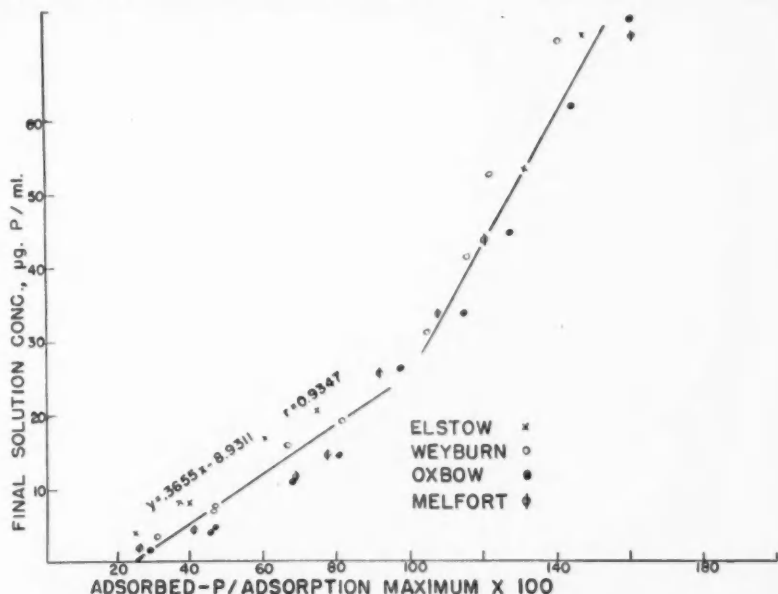


FIGURE 4. Relationship between final solution concentration and percentage saturation of the adsorption maximum.

Extraction Studies

These studies were undertaken to facilitate a comparison between adsorbed phosphorus and phosphorus extracted with carbonated water. A comparison between phosphorus added in solution and extractable phosphorus is afforded in Figure 5. The CO_2 extractable data have been corrected for the amount of phosphorus originally present in the soil. The data show a straight line relationship between added and extractable phosphorus until over 80 p.p.m. of phosphorus was added. (Above this point the curves tend to level off). The carbonated water removed from the soils a certain fixed fraction of the amount of phosphorus added. The low extraction of the added phosphorus from the Elstow soil is due to the low amount of phosphorus adsorbed from solution, whereas the reverse is true for the Melfort soil. The intermedial slopes of the Weyburn and Oxbow soils can similarly be explained.

The relationship between adsorbed phosphorus and extractable phosphorus is given in Figure 6. There is a straight line relationship between the two variables for each soil but, between soils, little correlation is apparent. However, where extractable phosphorus is corrected for the amount of extractable phosphorus present in the soil initially, the separate straight lines for each soil (Figure 6) join to form a reasonably close relationship between adsorbed phosphorus and CO_2 extractable phosphorus (Figure 7). While the CO_2 extraction removed an average 76 per cent of the adsorbed phosphorus, the percentage varied somewhat between soils.

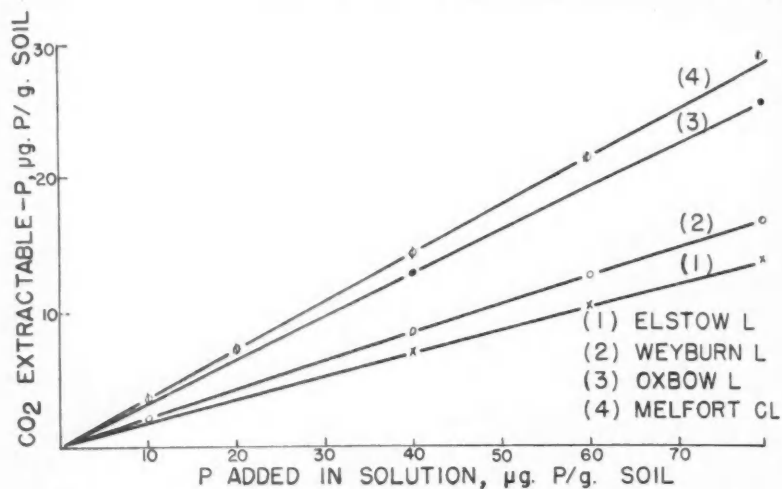


FIGURE 5. CO₂ extractable-P in soils that had been equilibrated for six hours with water solutions of increasing P concentration.

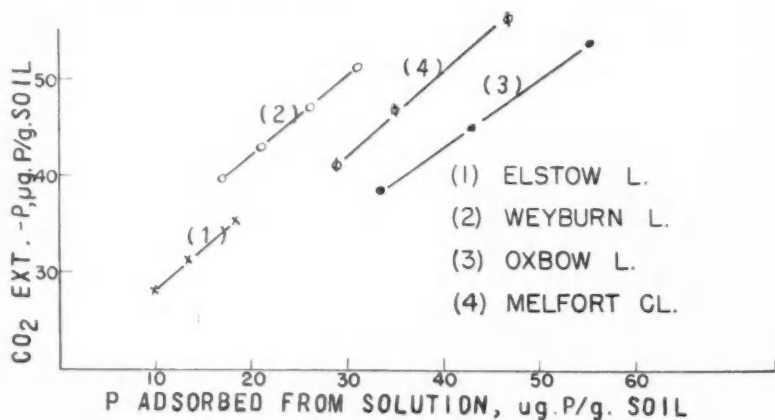


FIGURE 6. The relationship between CO₂ extractable-P and P adsorbed from solution.

DISCUSSION

The primary object in defining the form of phosphorus in soils is to be able to predict the pattern of phosphorus supply to growing plants. The data presented here suggest that the addition of phosphorus to the four soils (in amounts not divorced too greatly from those experienced under field conditions) is probably not fixed as is commonly thought (12), but is adsorbed as a mono-molecular layer on the surface of the soil colloids. The primary evidence presented for such adsorption is the close agreement

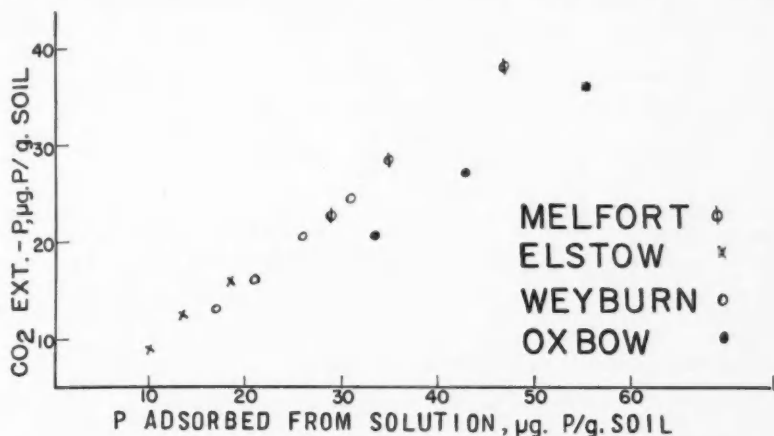


FIGURE 7. The relationship between CO₂ extractable-P (corrected for extractable-P in the untreated soil) and P adsorbed from solution.

of the phosphorus adsorption data with the Langmuir isotherm. It should be noted that such agreement does not necessarily imply an adsorption reaction, since the application of this equation for the adsorption of ions by solids requires further verification. The equation has been applied to adsorption of ions by solids (2, 7) although the theoretical basis is not as specific as for gas adsorption on solids.

Total adsorbed phosphorus does not reflect the equilibrium concentration of phosphorus in a soil suspension since at any one final solution concentration a range of adsorbed phosphorus values were obtained, depending on the characteristics of the soil used. Similarly, it would appear that surface phosphorus measurements alone are not proportional to the 'available' or equilibrium concentration of phosphorus. Fried and Shapiro (5) pointed out that a capacity factor, or the ability of the soil to continue to supply phosphorus to the soil solution, should be evaluated. The data presented here suggest that the percentage saturation of the adsorption maximum may serve as a measure of the capacity of the soil to supply phosphorus to the soil solution. In addition, the close relationship between the percentage saturation of the adsorption maximum and the final solution concentration (Figure 4) suggests that the equilibrium concentration of phosphorus in a soil suspension may be used to estimate the degree of saturation of phosphorus on the soil colloids. These variables are related by the equation $y = 0.366x - 8.931$, where y = the equilibrium concentration of P in p.p.m. and x = the percentage saturation of the adsorption maximum.

Carbonated water extractable phosphorus has been shown to be closely related to the amount of adsorbed phosphorus present on the four soils. The CO₂ extractions removed an average of 76 per cent of the adsorbed phosphorus; the percentage of removal varied somewhat depending on the soil, e.g., 88, 73, 63 and 80 per cent of the adsorbed phosphorus was

removed by carbonated water from the Elstow, Weyburn, Oxbow and Melfort soils, respectively. An attempt to relate the CO_2 extractable values to the percentage phosphorus saturation of the adsorption maximum was made with little success. This would indicate that the CO_2 extraction does not measure the ability of the soil to supply phosphorus to the soil solution, but rather removes a definite amount of total adsorbed phosphorus.

Olsen and Watanabe (13) have shown that the adsorption maximum correlates closely with the total surface area of soils as measured by ethylene glycol retention. While specific surface measurements were not carried out on the four soils used, it would appear from Table 1 that the soils, arranged in order of increasing clay and organic matter content—Elstow, Weyburn, Oxbow and Melfort, also fall in a similar order of increasing adsorption maxima. The organic matter appears to be equally as important as the clay in determining the adsorption capacity of the soil. The Weyburn and Oxbow loam soils contained identical amounts of clay but the total nitrogen content of the latter soil was 45 per cent higher; the adsorption maximum of the Oxbow soil was approximately 70 per cent larger than that obtained on the Weyburn soil. Similar comparisons between the Weyburn and Elstow soils also indicate the high adsorptive capacity of the organic fraction in the soils. Differences in exchangeable Ca^{++} between the soils are not in general related very closely to the adsorption maximum obtained on the respective soils, i.e., the Weyburn soil contained 2.5 times as much exchangeable Ca^{++} as the Elstow soil, but the difference between the respective adsorption maxima is small.

The average values of the constant k , derived from the slope and intercept values, are .077, .125, .201 and .160 for the Elstow, Weyburn, Oxbow and Melfort soils respectively. As the value of the constant increases, the bonding energy of the soil for phosphorus increases. Thus, the soils high in organic matter (Black soils) may hold the phosphorus with greater bonding energy than the Dark Brown soils. However, the constant k is markedly affected by experimental error, and little weight can be placed on the difference obtained. The average value obtained for the four soils, .141, is lower than the 0.92 value reported by Olsen (13) for soils with an alkaline pH.

ACKNOWLEDGEMENTS

The financial assistance afforded by the Consolidated Mining and Smelting Company of Canada Limited, and the guidance and advice given by W. L. Hutcheon throughout the investigation, are gratefully acknowledged.

REFERENCES

1. Boischot, P., M. Coppenet, and J. Hebert. Fixation de l'acide phosphorique sur le calcaire des sols. *Plant and Soil* 2:311-322. 1950.
2. Boyd, G. E., J. Schubert, and A. W. Adamson. The exchange adsorptions of ions from aqueous solutions by organic zeolites. Ion exchange equilibria. *J. Amer. Chem. Soc.* 69:2818-2829, 1947.
3. Cole, C. V., S. R. Olsen, and C. O. Scott. The nature of phosphate sorption by CaCO_3 . *Soil Sci. Soc. Amer. Proc.* 17:352-356. 1953.

4. Davis, L. E. Sorption of phosphates by non-calcareous Hawaiian soils. *Soil Sci.* 40:129-158. 1935.
5. Fried, M., and R. E. Shapiro. Phosphate supply pattern of various soils. *Soil Sci. Soc. Amer. Proc.* 20:471-475. 1956.
6. Glasstone, S. Textbook of physical chemistry. 2nd ed. D. Van Nostrand Co. Inc., Toronto, Ont. 1953.
7. Graham, D. R. The characterization of physical adsorption systems. I. The equilibrium function and standard free energy of adsorption. *J. Phys. Chem.* 57:665-669. 1953.
8. Kurtz, T., E. E. De Turk, and R. H. Bray. Phosphate adsorption by Illinois soils. *Soil Sci.* 61:111-124. 1946.
9. Langmuir, I. The adsorption of gases on plane surfaces of glass, mica, and platinum. *J. Amer. Chem. Soc.* 40:1361-1403. 1918.
10. McAuliffe, C. D., N. S. Hall, L. A. Dean, and S. B. Hendricks. Exchange reaction between phosphates and soils: Hydroxylic surfaces of soil minerals. *Soil Sci. Soc. Amer. Proc.* 12:119-123. 1947.
11. McGeorge, W. T. Phosphate availability in alkaline calcareous soils. *J. Amer. Soc. Agron.* 25:351-354. 1933.
12. Mass, E. F., and C. F. Bentley. Phosphorus fixation studies with some Saskatchewan soils. *Sci. Agr.* 26:275-287. 1946.
13. Olsen, S. R. and F. S. Watanabe. A method to determine a phosphorus adsorption maximum of soils as measured by the Langmuir isotherm. *Soil Sci. Soc. Amer. Proc.* 21:144-149. 1957.
14. Prutton, C. F., and S. H. Maron. Fundamental principles of physical chemistry. Macmillan Co., New York, N.Y. 1953.
15. Russell, G. C., and P. F. Low. Reactions of phosphate with Kaolinite in dilute solution. *Soil Sci. Soc. Amer. Proc.* 18:22-25. 1954.
16. St. Arnaud, R. J. A study of methods for measuring phosphate availability in Saskatchewan soils. M. Sc. thesis, Univ. Sask. 1950.
17. Seatz, L. F. Phosphate activity measurement in soils. *Soil Sci.* 77:43-51. 1954.
18. Shelton, W. R., and H. J. Harper. A rapid method for the determination of total phosphorus in soil and plant material. *Iowa State Coll. J. Sci.* 40, 4:403. 1941.
19. Truog, E., and A. H. Meyer. Improvements in the Deniges colorimetric method for phosphorus and arsenic. *Ind. Eng. Chem. Anal. Ed.* 1:136-139. 1929.
20. Wiklander, L. Kinetics of phosphate exchange in soils. *Ann. Roy. Agr. Coll. Sweden* 17:407-424. 1950.

THE PELTIER EFFECT AND ITS USE FOR DETERMINING RELATIVE ACTIVITY OF SOIL WATER¹

H. C. KORVEN² and S. A. TAYLOR³

[Received for publication August 12, 1958]

ABSTRACT

An apparatus is described which involves the use of a small thermocouple, cooled to the dew point by the Peltier effect, as a means of determining the relative activity of water in soils.

Thermocouples were calibrated over a series of sulphuric acid solutions immersed in a constant temperature bath controlled to within 0.003°C. The temperature of the bath for all readings was 25°C. Readings were taken over Benjamin silty clay loam soil samples that had been brought to desired soil moisture relative activities by the pressure plate and pressure membrane methods. The following conclusions were reached:

1. The thermocouple technique shows promise as a laboratory procedure for determining the relative activity of water in soils.
2. The majority of the results showed a gradual lowering of the readings with time. This was overcome at the expense of speed by treating the thermocouple with a plastic spray paint.
3. More study and testing are required before the technique can be considered a completely satisfactory procedure.

INTRODUCTION

The principle of operation of methods for determining the availability of soil water to plants can best be described by the relative activity concept of soil water. The relative activity of soil water is the ratio of water vapour pressure of soil to that of pure free water at the same temperature and pressure. It is dependent upon the osmotic potential and the energy required to remove a unit mass of water from the soil which is related to the availability of the water to growing plants. Instruments such as the porous electrical resistance unit, tensiometer, pressure plate, and pressure membrane can be used to determine this characteristic under some conditions, but none is completely satisfactory. The main disadvantage of methods at present available is that the effect of salt (osmotic potential) is not measured. Other disadvantages are that neither of the first two instruments mentioned adequately covers the complete range of soil moisture important in plant growth, and the latter two are limited to laboratory use. The thermocouple technique, employing the Peltier effect⁴, shows promise because it determines the total potential as shown by Spanner (5) for the determination of "suction pressure" in plant material. The objective of this study, therefore, was to determine the possibilities of using the thermocouple technique for determining the relative activity of water in soil.

¹ Adapted for publication from a thesis submitted to the Graduate School, Utah State University, Logan, by the senior author in partial fulfillment of the requirements for the degree of Master of Science in Irrigation Science. Joint contribution from the Field Husbandry, Soils and Agricultural Engineering Division, Experimental Farms Service, Canada Department of Agriculture, Ottawa, and the Utah Agricultural Experiment Station, Logan, Utah, U.S.A. Approved for publication by the Utah Agricultural Experiment Station as *Journal Article No. 47*.

² Agricultural Engineer, Experimental Farm, Swift Current, Saskatchewan.

³ Professor of Soil Physics, Utah State University, Logan, Utah.

⁴ Peltier effect is defined by Merriman and Wiggan (2) as follows: "When a circuit is made up of two dissimilar metals and the two junctions are maintained at different temperatures, an e.m.f. will be established which will be very nearly proportional to the difference in temperature between the two junctions. Conversely, if current is passed through a circuit consisting of two dissimilar metals, heat will be developed at one junction and absorbed at the other junction. This is known as Peltier effect."

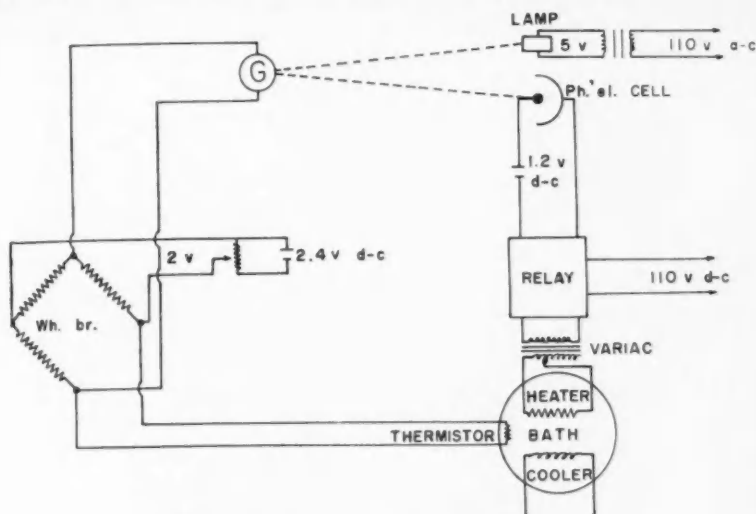


FIGURE 1. Bath temperature control circuit.

REVIEW OF LITERATURE

Richards* has also been exploring the possibilities of using the thermocouple technique. The two techniques, however, differ in two respects. Richards wets one junction by dipping it in water, whereas the technique described in this study wets the one junction by cooling it below the dew point by the Peltier effect. Richards used a "Chromel P"-constantan thermocouple while the authors used a bismuth-bismuth 5 per cent tin thermocouple with thermoelectric potentials of 63 and 126 microvolts per degree Centigrade, respectively.

On completion of the study reported herein it was interesting to learn that the workers at the Rothamsted Experimental Station (4) had also been studying the possibilities of adapting to soils the thermocouple technique employed by Spanner for determining the suction pressure of plant material. This report describes a bismuth-chromel thermocouple which determines "very accurately the Relative Humidity of the atmosphere in equilibrium with a sample of soil in a small sealed vessel". They are, however, still experiencing some difficulty with calibration and stray electromotive forces. They conclude that "Temperature stability is absolutely essential, and there is little prospect of the method being much use in the field".

APPARATUS

Temperature Control and Measurement Apparatus

The main problem in the design of the apparatus was the very fine degree of temperature control and measurement required. Spanner (5) points out that a solution with an osmotic pressure of 80 atmospheres

*Richards, L. A. Personal communication.

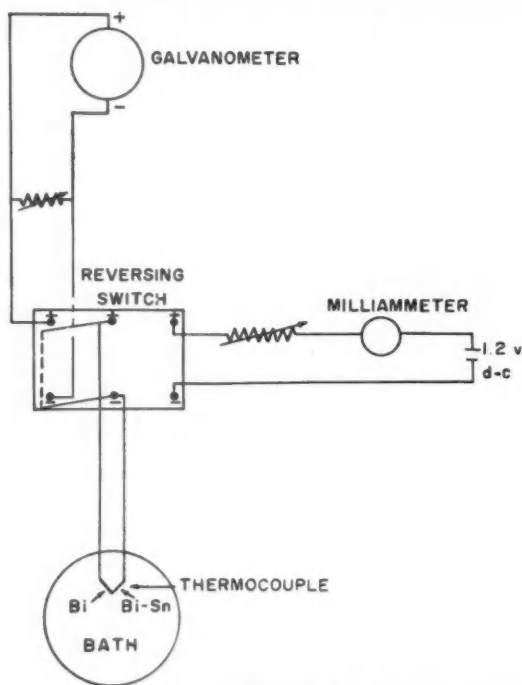


FIGURE 2. Measuring circuit.

depresses the dew point temperature only 1°C . Therefore, to measure the osmotic pressure to within 0.1 atmospheres it is necessary to control and measure the temperature to within 0.001°C .

The main components of the equipment are the controlled temperature bath, the temperature control circuit, and the measuring circuit.

A bath designed for freezing point determinations which is similar to that described by Richards and Campbell (3) was used. The refrigerator unit runs continuously while the heater is turned off and on. The rates of heating and cooling can be adjusted to obtain the desired degree of balance.

The circuit for controlling the temperature of the bath is shown in Figure 1.

One part of the circuit consists of the thermistor, which serves as the temperature detecting element, mirror galvanometer and power source connected to a Wheatstone bridge. The other part of the circuit consists of the photoelectric cell that energizes the electronic power relay, which in turn switches the bath heater on and off. The beam of light is focused on the mirror of the galvanometer and the reflected light connects the two circuits when it shines on the photoelectric cell located one metre away.

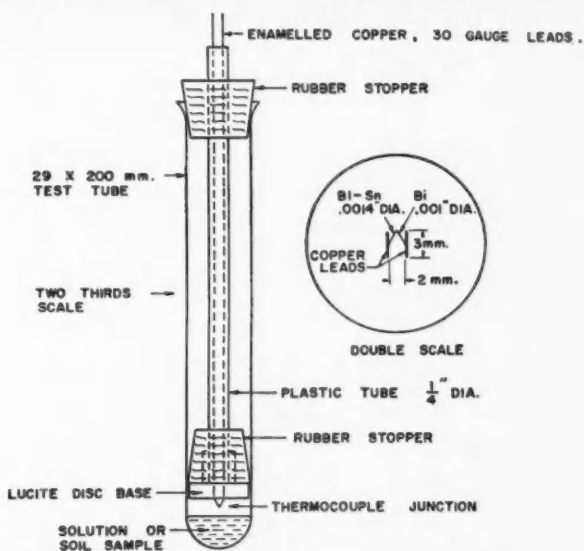


FIGURE 3. Sketch of thermocouple assembly and enlarged view of junction.

The variation in bath temperature was approximately 0.003°C . This variation is greater than the allowable 0.001°C . cited by Spanner. The temperature variation of the atmosphere in the test-tube, however, was within the sensitivity of the measuring apparatus because no noticeable motion of the galvanometer was detected as the heating element turned on and off.

The circuit for determining the relative activity of water is shown in Figure 2. This is a simple circuit, consisting of a regulated power source, reversing switch, galvanometer, and the thermocouple assembly which was immersed in the bath. This circuit is also in two parts. One part consists of the thermocouple assembly, variable resistance, milliammeter, and power source. The other part consists of the thermocouple and the galvanometer. The reversing switch connects the thermocouple with the two circuits.

The Thermocouple

The thermocouple assembly and enlarged view of the junction are shown in Figure 3. The basic components—the size and type of lead and junction wires—are the same as described by Spanner (5). The design, however, was modified so that the thermocouple assembly would fit into the test tube of the constant temperature bath.

The technique used in handling and soldering the fine junction wires is described by Strong (6). The most difficult phase in the construction of a reliable thermocouple proved to be the removal of excess flux (a saturated solution of zinc chloride). Two cleaning procedures were used—a

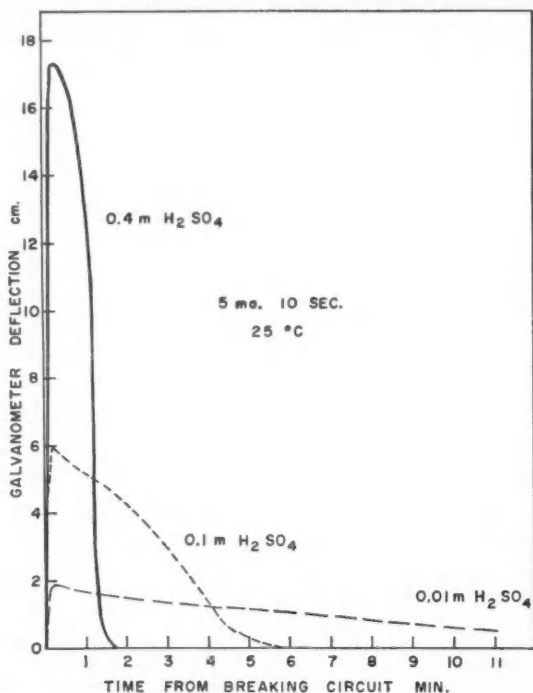


FIGURE 4. Cooling Curves—Thermocouple over sulphuric acid solutions.

spray of distilled water from a plastic squeeze bottle, and soaking in several changes of distilled water and detergent. The spray seemed to be the more satisfactory, but not always.

The thermocouple is first connected to the power source and a pre-determined current is passed through it in such a direction as to cool the free junction* below the dew point. The maximum cooling obtained with the junction used was 4.9°C . Moisture condenses on the cool junction which, in effect, means that the thermocouple behaves as a delicate wet-bulb thermometer since the other pair of junctions remains dry at ambient temperature. The thermocouple is then switched immediately to the galvanometer by means of the reversing switch. The galvanometer swings to a maximum deflection corresponding to the dew point temperature depression. As the free junction warms to ambient temperature, the condensed water evaporates, which causes the e.m.f. to decrease steadily and the corresponding galvanometer deflection to return to zero.

The general performance of the thermocouple is shown in Figure 4. The curves are labelled *cooling* curves because they record the galvanometer reaction after cooling the junction. This figure shows that, as the relative

* The free junction is the junction of the two very fine wires, bismuth and bismuth 5 per cent tin. It follows, then, that the *warm* junction is the pair of junctions between the fine wires and the comparatively massive copper lead wires. The temperature of the pair of *warm* junction remains at ambient temperature because the heat developed is dissipated by the massive copper lead wires.

TABLE 1.—RELATIVE ACTIVITIES OF A SERIES OF H₂SO₄ SOLUTIONS

Approx. H ₂ SO ₄ conc.	Actual H ₂ SO ₄ conc.	a _w [°] at 25°C. ¹
m ²	m	
0.01	0.010	0.9995
0.02	0.016	0.9993
0.05	0.050	0.9980
0.10	0.094	0.9965
0.20	0.179	0.9935
0.30	0.277	0.9901
0.40	0.369	0.9867

¹ Relative activities were picked off a curve obtained by plotting values given by Kortüm and Bockris.² Molality.

activity of water is increased, as shown by a decrease in concentration of sulphuric acid, the maximum deflection is decreased and the time required for the galvanometer to return to zero is increased. For example, near saturation, depicted by the dilute solution of 0.01 molal (m) sulphuric acid (pure water has the highest relative activity), the maximum deflection is 1.9 centimetres and the time to return to zero is more than 11 minutes. Comparable figures for the 0.4 m solution are 17.2 centimetres and less than 2 minutes. The relative activities of these solutions are equivalent to about field capacity (0.01 m) and permanent wilting percentage (0.4 m).

PROCEDURE

Calibration of the Thermocouple

The thermocouple was calibrated over a series of solutions of sulphuric acid. All readings recorded were at a bath temperature of 25° C. The selection of molalities to give the desired vapour pressure was determined from Kortüm and Bockris (1). The actual molality was determined by titrating against sodium carbonate. The titrations were conducted in triplicate and the results are recorded in Table 1.

Thermocouple Readings over Soil Samples

The procedure for obtaining readings over soil samples was similar to the procedure used for calibrating the thermocouples.

A series of relative activities of soil water assuming salt free soil was established by the pressure plate and pressure membrane methods (7). Benjamin silty clay loam was used.

The relative activities corresponding to the various pressures were calculated according to the formula:

$$\Delta P = - \frac{RT}{\bar{V}} \ln \frac{P}{P_0}$$

Where ΔP is the difference in pressure between inside and outside the apparatus in atmospheres.

R is the universal gas constant or 82.057 cm.³ atm. per ° C. per mole.

T is the absolute temperature or 298.16°K at 25°C.

\bar{V} is the partial molar volume at 25°C. or $\frac{18.016}{0.99740} = 18.069$ cm.³ per mole.

p is the water vapour pressure of soil.

p_0 is the vapour pressure of pure free water at the same temperature and pressure.

$\frac{p}{p_0}$ is the relative activity of the soil water.

The values obtained are shown in Table 2.

TABLE 2.—RELATIVE ACTIVITIES OF SOIL WATER AT
A SERIES OF PRESSURES IN THE PRESSURE
PLATE AND PRESSURE MEMBRANE

ΔP	a_w^1
atm.	
0.33	0.9998
1.25	0.9991
2.50	0.9982
5.0	0.9963
10.0	0.9925
15.0	0.9889

¹ The relative activity of the soil water

RESULTS AND DISCUSSION

Fifteen thermocouples were constructed during the study. Readings from only one thermocouple, however, are reported. A large number of readings were taken with other thermocouples but have not been included because:

1. The fragility of the thermocouple made it difficult to obtain a complete set of readings before failure.
2. All thermocouple readings showed the same gradual lowering trend which will be discussed later. It was not possible, however, to combine data because of variation in the magnitude of the readings between thermocouples.
3. Some thermocouples produced very erratic readings because all the flux had not been removed.

The discussion, however, where applicable, is based on the experience gained with other thermocouples as well as for the one for which data are reported.

Calibration of the Thermocouple

Figure 5 shows the relationship between maximum galvanometer deflection and the relative activity of water in sulphuric acid solution; the number attached to each reading indicates the date of the month. The straight line calibration curve was obtained only when the whole range was covered with a minimum number of readings, one at either end of the range and one in the middle. This reading procedure was adopted after having experienced a lowering of readings with previous thermocouples similar to that shown by readings on dates 7, 13, and 23 in Figure 5.

The series of readings over the 0.4 molal solution in Figure 5 shows that this trend can be stopped by thoroughly drying the thermocouple. The reading (21st) which falls above the curve was taken after the thermo-

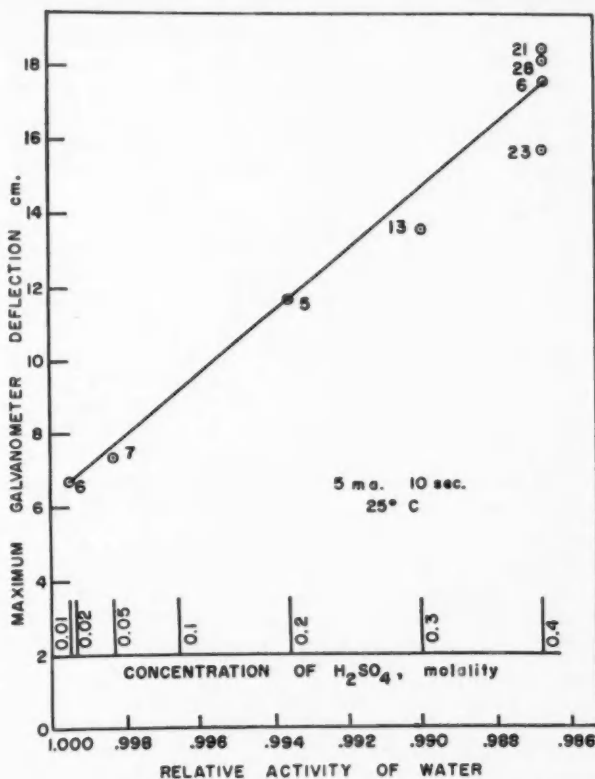


FIGURE 5. Relationship between maximum galvanometer deflection and relative activity of water in H_2SO_4 solutions.

couple had remained in room atmosphere for 6 days. To check this apparent drying effect, two more readings were taken over the same solution. The thermocouple was left sealed over the solution for an additional 2 days and a reading taken (23rd) which is below the curve. The thermocouple was then exposed again to room atmosphere for 5 days and a reading taken (28th) which is also above the curve.

Thermocouple Readings over Soil Samples

Readings were taken over soil samples during the time interval from dates 7th to 13th, using the same thermocouple as that in Figure 5 even though the thermocouple was not completely satisfactory. Figure 6 records readings over soil samples, together with comparable readings over solutions taken from Figure 5. The calibration curve of Figure 5 has also been added for reference. Figure 6 shows that the thermocouple readings over soil samples were similar in magnitude to those over solutions, and also the similar lowering trend discussed in Figure 5.

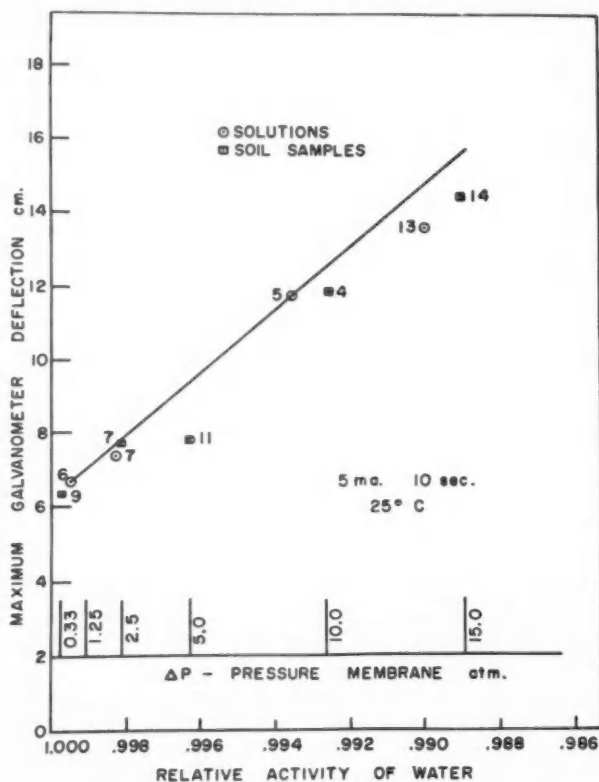


FIGURE 6. Relationship between maximum galvanometer deflection and relative activity of water in H_2SO_4 solutions and soil.

Readings after Treating the Thermocouple

In an attempt to overcome the apparent gradual wetting of the thermocouple a plastic treatment was explored. This treatment consisted of spraying the thermocouple used in Figures 5 and 6 with a clear plastic spray paint labelled "Spraint Ignition Sealer".

Readings were taken over 0.4 and 0.01 molal solutions and the data are recorded in Table 3.

* Minit Spray Corp., Chicago, Ill.

TABLE 3.—EQUILIBRIUM READINGS—SECOND THERMOCOUPLE AFTER PLASTIC TREATMENT

H_2SO_4 Conc.	Maximum galvanometer deflection		
	1st run	2nd run	3rd run
m	cm.	cm.	cm.
0.4	18.7 to 18.9	19.0	19.2
0.01	3.5	3.5	

The data in Table 3 show that treating the thermocouple has overcome the trend of readings gradually lowering as shown in Figures 5 and 6. An additional indication that the plastic spray had made the thermocouple more stable was that the readings stayed constant for a longer period than when it was untreated. Before treatment it was only rarely that a constant reading was obtained for a period of more than 2 hours. After treatment, however, it was not uncommon to record the same reading for a period of 5 or 6 hours. In the case of the reading over the 0.01 molal solution the same reading was recorded over a period of 9 hours. This treatment has, however, increased the time required to attain equilibrium readings; before treatment the readings levelled off in about 12 hours, whereas after treatment the time required was about 24 hours.

Table 3 provides a limited amount of information for evaluating the thermocouple technique. The precision of the technique is about 1 per cent, based on the readings over the 0.4 molal solution which showed more variation. This figure is conservative because it was not uncommon throughout the study for duplicate readings, taken within a matter of minutes, to be identical. The thermocouple is estimated to measure the relative activity of water to within an accuracy of about .0003.

CONCLUSIONS

A small thermocouple cooled by the Peltier effect shows promise for determining the relative activity of soil water in the range between permanent wilting percentage and field capacity.

The most important single factor in constructing a successful thermocouple is to remove all trace of excess flux (zinc chloride).

Treating the thermocouple with plastic spray eliminates drift and makes the instrument more stable, but the time required to reach equilibrium is increased.

The thermocouple determines relative activity of soil water and of sulphuric acid solutions with the same accuracy.

Further improvements in design of the thermocouple are required before the technique will be a completely satisfactory laboratory procedure. For example, until the time required to reach equilibrium is shortened the technique will be limited in its use because of the precise temperature control required.

REFERENCES

1. Kortüm, G., and J. O'M. Bockris. Textbook of electrochemistry. Elsevier Press, New York, N.Y. 1951.
2. Merriman, Thaddeus, and Thos. H. Wiggin. American civil engineers' handbook. John Wiley & Sons, Inc., New York, N.Y. 1945.
3. Richards, L. A., and R. B. Campbell. Use of thermistors for measuring the freezing point of solutions and soils. *Soil Science* 65:429-436. 1948.
4. Rothamsted Experimental Station. Report of Rothamsted Experimental Station for 1956, pp. 38 and 87. Richard Clay & Co., Ltd., Bungay, Suffolk. 1957.
5. Spanner, D. C. The Peltier effect and its use in the measurement of suction pressure. *J. Exptl. Botany* 2:145-168. 1951.
6. Strong, John. Procedures in experimental physics. Prentice-Hall, Inc., New York, N.Y. 1946.
7. U.S. Salinity Laboratory Staff. Diagnosis and improvement of saline and alkali soils. U.S.D.A. Handbook 60, Washington, D.C. 1954.

